The Design, Application and Evaluation of a Gamified Virtual Laboratory to Aid in Distance Learning.

Tauber, Amanda L; Schweiker, Stephanie S; Levonis, Stephan M

QUEENSLAND ANNUAL CHEMISTRY SYMPOSIUM

QUT

School of Chemistry and Physics

27th of November 2020

at QUT (Gardens Point)

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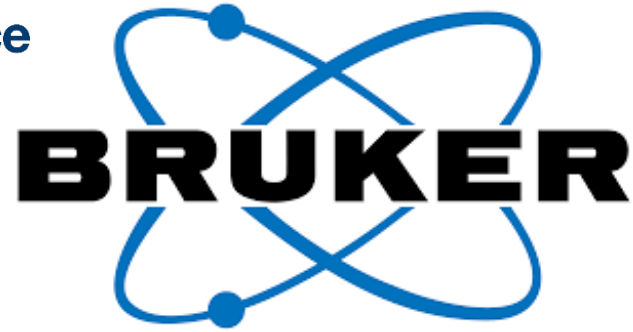

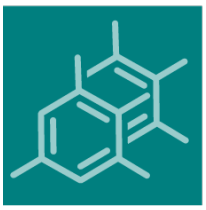

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GROUP

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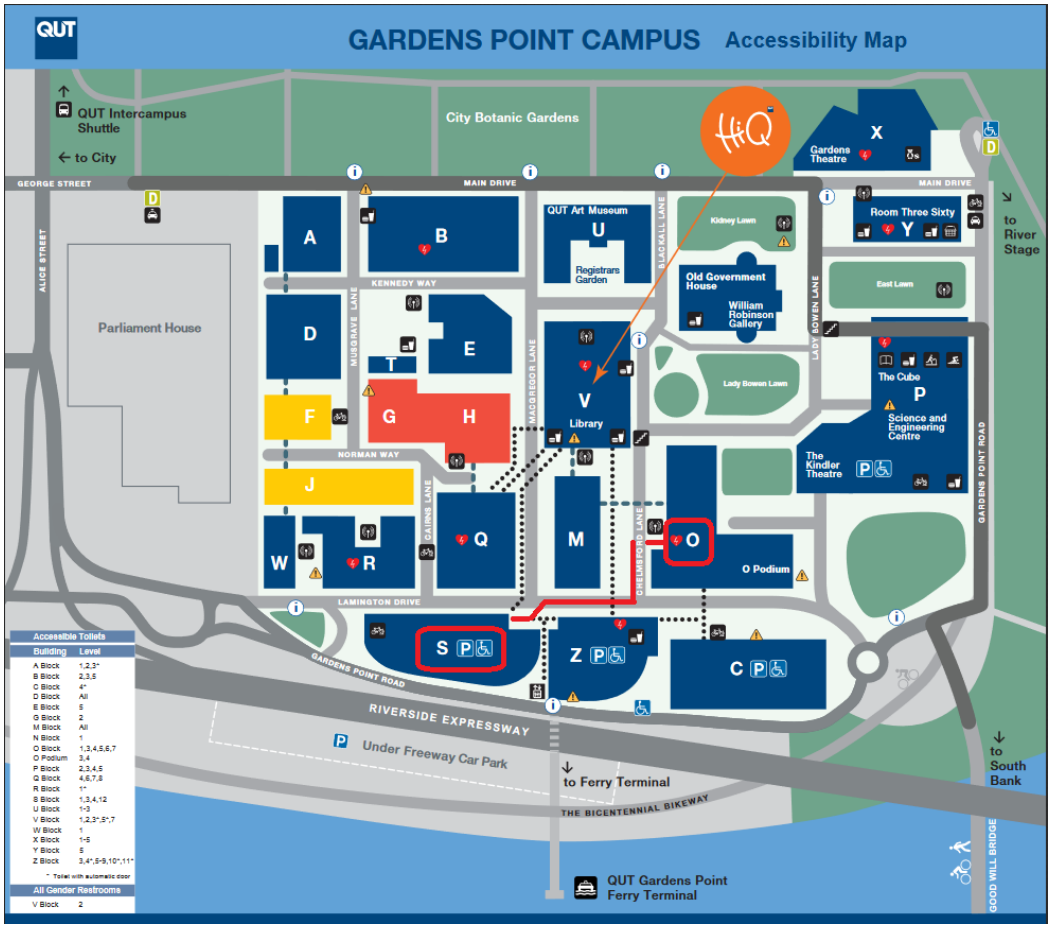
Overview timeplan:

8:00 AM	Reception (O block, room 134)
8:40 AM	Opening remarks (S block, rooms 403, S410, S636/7)
8:45 AM	Plenary session Dr Carol Hua
9:30 AM	Morning tea
10:00 AM	Morning session A - D
12:00 PM	Lunch break
1:15 PM	Plenary session Prof Gwen Laurie
2:00 PM	Afternoon session E - H
3:30 PM	Afternoon tea
4:00 PM	Plenary session Dr Bryan Tuten
4:45 PM	Closing remarks
5:00 PM	Social event (Botanical Bar)

Live sessions for the plenary talks will be in S403 and streamed in S410, S636/7. Please find the venues for the streams below in the timetable.

Morning tea, lunch break, and afternoon tea will be served in O block, room 134.



Zoom link for the sessions:

Plenary session Dr Carol Hua:
https://qut.zoom.us/j/85732401802?pwd=NGpGdG5wb1luc0Jvb1FKbExtQ2FoQT09
Password: 278879

Plenary session Prof Gwen Laurie
https://qut.zoom.us/j/84826003862?pwd=N1M4OUZ6K25leGJFTWF5VUNSYThTdz09
Password: 099013

Plenary session Dr Bryan Tuten
https://qut.zoom.us/j/83180843836?pwd=dU8yaDVwQzEzcStOaE1kN1JwSDNJQT09
Password: 703928

Stream A (Analytical Chemistry)
https://qut.zoom.us/j/89631242727?pwd=eEdyRlJUNU40dC96ZGRrY1R1aFE2UT09
Password: 275952

Stream B (Medicinal and Chemical Biology)
https://qut.zoom.us/j/88250419308?pwd=cTFBT0tFUVc5Z0hibExUcjB3S1c1UT09
Password: 940290

Stream C (Environmental Chemistry and Natural Products)
https://qut.zoom.us/j/82560590420?pwd=N3ZxSHg0U1lSaVIrVWZKMEc4UHZOQT09
Password: 408812

Stream D (Nanomaterials, Computational and Electrochemistry)
https://qut.zoom.us/j/85935900558?pwd=ZEE0b205Z3FXT0xFRzlkSGJacGNWZz09
Password: 610587

Stream E (Polymer and Photochemistry)
https://qut.zoom.us/j/88136227313?pwd=SGtMWE4wcGNBS0dJNXY0VnhVMnVHdz09
Password: 524851

Stream F (Inorganic Chemistry and Crystallography)
https://qut.zoom.us/j/87907374898?pwd=ZUIrNUhQOUxDUmVLRW1yclR0ZXJ5Zz09
Password: 665606

Stream G (Education and Organic Chemistry)
https://qut.zoom.us/j/82329096750?pwd=eHpqWFlPUjZHRGxLT01XVVQ3WkxGUT09
Password: 028400

Stream H (Medicinal, Polymer and Physical Chemistry)
https://qut.zoom.us/j/84790274300?pwd=TFl5ckZBUllsWXRXbTBxU0J5OUJYUT09
Password: 955065

Registrations will commence from 8:00 am	
Morning Plenary Session – Chair: Dr. Michael Pfrunder	
8:40	**Opening remarks: Dr. Michael Pfrunder**
8:45	**Plenary Lecture P1: Dr. Carol Hua – Chair: Dr. Michael Pfrunder** *Coordination Polymers as Chiral Probes and Sensors*
9:30	**Morning Tea**
Morning Parallel Sessions	
	Analytical Chemistry – Chair: Ena Luis **Venue: S636**
10:00	A1 - **Mahnaz Gholami** *A novel SERS-biosensor for determination of protein biomarkers*
10:15	A2 - **Hung Trieu Hong** *Optimisation of extraction procedure and LC-DAD-MS methodology for anthocyanin analysis in pigmented corn kernels*
10:30	A3 - **Tony Wang** *Calculation methods for Cellulose Crystallinity Index using X-ray Diffraction*
10:45	A4 - **E. M. Tanvir** *Application of an ICPMS method to determine nineteen clinical trace elements concentrations in whole blood and plasma: investigation of the effect of storage temperature*
11:00	A5 - **Justin Cormick** *The characterisation of novel precursor compounds for the production of illicit drugs by isotope ratio mass spectrometry*
11:15	A6 - **Paul Denman** *Agarose Encapsulated Vitamin B12a Coated Gold Nanoparticle Aggregates for pH modulated SERS Based Detection of Cyanides, Sulphur Dioxide & NOx Gases*
11:30	A7 - **Saiqa Muneer** *A Plasmonic recyclable nickel foam sensor for the therapeutic drug monitoring of Meropenem in blood by SERS*
11:45	A8 - **Hyo Jeong (Minnie) Kim** *Development and Application of Method to Analyse the Sialylation of the Cells*
11:50	A9 - **Zhi Hung Loh** *Identification of volatile plant compounds in Pimelea trichostachya responsible for livestock aversion*
11:55	A10 - **David Marshall** *Manipulating redox-active supramolecular complexes by mass spectrometry*
12:00	*End of Session*
	Biology and Medicinal and Chemical Biology – Chair: Vito Ferro **Venue: S637**
10:00	B1 - **Julia Kurz** *Structure activity relationship study of ketol-acid reductoisomerase inhibitor NSC116565*
10:15	B2 - **Harrison Madge** *Structure–Activity Analysis of A Self-Adjuvanting Cyclic Multicomponent Lipopeptide Delivery System for Group A Streptococcus Peptide Antigens*
10:30	B3 - **Sara Motamen** *Analysis of Approaches to Anti-tuberculosis Compounds*

Morning Parallel Sessions cont.	
10:45	B4 - **Jianying Han** *Exploring the potential of endophytes and fungi as sources of antimicrobial compounds*
11:00	B5 - **Charles Dai** *Application of polyethylenimine as an intranasal adjuvant for intranasal group A Streptococcus vaccine*
11:15	B6 - **Jessica Harris** *Interrupting the Conversation: In Silico Design of Dual Acting Quorum Quenching Agents*
11:30	B7 - **Duy Than Nguyen** *Identification of Potential Chemical Probes from Macleaya cordata (Willd) R. Br.*
11:35	B8 - **Caleb Kam** *In-silico family-wide profiling of the poly (ADP-ribose) polymerase superfamily*
11:40	B9 - **Rimjhim Agarwal** *Selecting orange Capsicum as a source of dietary zeaxanthin*
11:45	B10 - **Asmaa Mahmoud** *Design and synthesis of rhamonosyl glycotope to protect against streptococcus pyogenes*
11:50	B11 - **Taylor Garget** *Deciphering selectivity and divergent responses in boronolectin fluorophores*
11:55	B12 – **Nedaa Ali Alharbi** *Intranasal Vaccination with a Lipopeptide-anchored Liposomes Vaccine Candidates against Streptococcus Pyogenes*
12:00	*End of Session*
	Environmental Chemistry & Natural Products – Chair: Laura Delafresnaye Broqua **Venue: S410**
10:00	C1 - **Shamsunnahar Kushi** *Applying Molecular Networking to Natural Products Chemistry*
10:15	C2 - **Fahad Ahmed** *How wastewater analysis be used as a tool to measure the population treated pain burden?*
10:30	C3 - **Elvis Okoffo** *Release of Plastics to Australian Land from Biosolids End-Use*
10:45	C4 - **Qiuda Zheng** *Development and validation of a method for metformin and oxypurinol in wastewater samples*
11:00	C5 - **Taizong Wu** *Discovery of New Pyranonaphthoquinones from an Australian Terrestrial Bacterium CMB-PB42*
11:15	C6 - **Kaumadi Samarasekera** *Investigation into the Chemical Transformation of Enterocin from Australian Soil Derived Streptomyces spp.*
11:30	C7 - **Cameron Johnston** *Resource Recovery from Acid Mine Drainage*
11:35	C8 - **Alexandra Gulizia** *Chemical digestion methods: what are the real impacts on microplastics?*

Morning Parallel Sessions cont.	
11:40	C9 - **Stephen Burrows** *Characterising weathered microplastics to better understand their sorption behaviour in the environment*
11:45	C10 - **Amila Agampodi Dewa** *Isolation of new microbial natural products using Global Natural Product Social (GNPS) molecular networking approach*
11:50	C11 - **Vivienne Santiago** *Bioactive Natural Product Prioritization in Venomous Animals Microbial Collections Using Multi-informational Feature-based Molecular Networks*
11:55	C12 – **Dushanthi M. Wanninayake** *A study of PFOA destruction using Combined Ultrasonication (US) and Advanced Oxidation Processes (AOP) involving Ozone (O3) - (US/O3 system).*
12:00	*End of Session*
	Nanomaterials, Computational & Electrochemistry – Chair: Tenille Herd **Venue: S403**
10:00	D1 - **Helapiyumi Weerathunga** *Photocatalytic benzyl alcohol oxidation using facet controlled ZnO nanocatalysts*
10:15	D2 - **Bayan Peelikuburage** *Photo-switchable product selectivity control in Aniline based synthesis*
10:30	D3 - **Marvin Gernhardt** *Multi-material 3D Microstructures with Advance Stimuli Responsive Properties*
10:45	D4 - **Shern Tee** *Fully Periodic Constant Potential Simulations of Electric Double Layers*
11:00	D5 - **Junxian Liu** *Theoretical Understanding of Electrocatalytic Hydrogen Production Performance of One-Dimensional Metal–Organic Frameworks*
11:15	D6 - **Mirella Santos** *Finite-size effects on the diffusion coefficients from molecular dynamics in crystal-like structures*
11:30	D7 - **Olawale Oloye** *Sonocatalytic Degradation/Conversion of Azo Dyes to Graphene Quantum Dots Using Liquid Metal Galinstan*
11:45	D8 - **Joan Zapiter** *Electrochemistry and X-ray Photoelectron Spectroscopy of Immobilized Proteins on Self-Assembled Monolayers on Gold Electrodes*
11:50	D9 - **Joshua Powell** *Effects of Lability and Melting Point on the Formation of Metal Oxide Phases Obtained by Calcination of Mixed-Metal Metal-Organic Frameworks*
11:55	D10 - **Samaneh Sadat Setayandeh** *First-principles study of the atomic volume of hydrogen in palladium*
12:00	*End of Session*
12:00	**Lunch**

1:15	**Plenary Lecture P2: Dr. Gwen Lawrie – Chair: Stephanie Schweiker** *Scaffolding Engagement and Capturing Student Thinking in Hybrid Learning Environments*
Afternoon Parallel Sessions	
	Polymer and Photochemistry – Chair: Marvin Gernhardt **Venue: S636**
2:00	E1 – **Alexandra L. Mutch** *Design of surface-functionalised polycaprolactone: considering degradation and fate of modified biomaterials*
2:15	E2 – **Hamish Poli** *Dewetting of poly(lactic-co-glycolic) Problems when modelling nanoparticles with thin films*
2:30	E3 – **Laura Delafresnaye** *Chemiluminescent Read-Out of Degradable Fluorescent Polymer Particle*
2:45	E4 – **Jessica Pelloth** *Wavelength-Gated Softening of Hydrogel Networks*
3:00	E5 – **Mohamaad Zaidur Rahman Sabuj** *Biodegradable Polymer Encapsulated Drug Nanoparticles for the Management of Lower Respiratory Tract Infections*
3:05	E6 – **Susanna Kunz** *Photo-Cross-Linkable Polymers for Inkjet Printed OLEDs*
3:10	E7 – **Kubra Kalayci** *Visible Light Induced Reversible Ligations for Precise Soft Materials Design*
3:25	E8 – **Philipp Kamm** *Photocycloadditions in Disparate Chemical Environments*
3:30	*End of Session*
	Inorganic Chemistry and Crystallography – Chair: Aidan Brock **Venue: S637**
2:00	F1 – **Isaac Etchells** *Exploring energy transfer in NIR emitting bimetallic d-f bisterpyridine complexes*
2:15	F2 – **Gina Quach** *Construction of enantiopure photoactive Ir(III)-containing tetrahedra*
2:30	F3 – **Matthew Allen** *A comparison of intra- vs intermolecular energy transfer between 4f metal ions using heteronuclear bimetallic supramolecular helicates*
2:45	F4 – **Jess Bilyj** *The Balancing Act of Stabilising High Oxidation States of Copper and Nickel with Redox Non-Innocent Ligands containing Thiosemicarbazone and Dithiocarbazate Schiff Bases*
3:00	F5 – **Amy Thompson** *Mechanistic Exploration of Elastically Flexible Crystals by Automatic Analysis*
3:15	F6 – **Max Coles** *Using Cu(I) for Earth Abundant Photocatalytic Metallo-Supramolecular Cages*
3:20	F7 – **Miguel Gonzalvez** *An Electrogenerated Organocopper(II) Reagent for the Formation of Carbon-carbon bonds*
3:25	*End of Session*

Afternoon Parallel Sessions cont.	
	Education and Organic Chemistry – Chair: Stephanie Schweiker **Venue: S410**
2:00	G1 – **Amanda Tauber** *The Design, Application and Evaluation of a Gamified Virtual Laboratory to Aid in Distance Learning*
2:15	G2 – **Joshua Reilly** *Mobilising molecular models across the COVID campus*
2:20	G3 – **Michael Pfrunder** *Zoomed-in Science: Connecting Real Scientists with Primary School Classes Over Zoom*
2:25	G4 – **Luke Churchman** *Understanding a stereoselective P450 epoxidation through a synthetic comparison*
2:30	G5 – **Matheus Carpinelli de Jesus** *Chemical composition of traditional medicine plants: D. obscura root bark*
2:35	G6 – **Michael Netzel** *Australian grown Feijoa (Acca sellowiana) – an underestimated fruit?*
2:50	G7 – **Natasha Hungerford** *Stingless bee honey as a unique source of trehalulose*
3:05	G8 – **Nicholas See** *Explorations into a new synthetic route to L-hexoses*
3:20	G9 – **Sandra Wiedbrauk** *Dual-Wavelength Gated oxo-Diels-Alder Photoligation*
3:25	G10 – **Joel Johnson** *Gingerol, Shogaol and Paradol: The Chemistry of Pungent Ginger Constituents*
3:30	G11 – **Alaa Saqer** *Characterizing the structure, bioactivity and bioavailability of active compounds from complex herbal extracts*
3:35	*End of Session*
	Physical Chemistry, Medicinal and Chemical Biology and Polymer Chemistry – Chair: Jasmine Jensen **Venue: S403**
2:00	H1 – **Krystina Lamb** *The problem of pore size determination; a comparison of techniques on a commercial templated porous silica*
2:05	H2 – **Lubna Naheed** *Determination of hydrogen adsorption density in porous/activated carbons at very high pressure and room temperature*
2:10	H3 – **Yichao Jin** *Tuning surface configuration of AgPd alloy catalysts to promote low temperature 5-hydroxymethyl-furfural oxidation*
2:15	H4 – **Mostafa Kamal Masud** *Mesoporous Gold Biosensor for Electrochemical Detection of MicroRNA at Attomolar Level*

Afternoon Parallel Sessions cont.	
2:20	H5 – **Wanli Jin** *Development of Tyrosinase Inhibitors as Potential Anti-melanoma Agents*
2:25	H6 – **Kah Yean Lum** *Chemical and Biological Investigations of Australian Crinoids*
2:30	H7 – **Louise Friberg** *Discovery and Development of Novel Antimicrobial Agents Using an Open-Access Database*
2:35	H8 – **Raghu Bolisetti** *Synthesis of novel antibiotic Octapeptin derivatives against Gram-negative bacteria*
2:40	H9 – **Ras Baizureen Roseli** *Thiol addition to naturally occurring Michael acceptors: What influences reactivity?*
2:45	H10 – **Ali Qaitoon** *Manganese Dioxide-based Responsive Nanoprobe for Glutathione Detection*
2:50	H11 – **Sadia Chowdhury** *A New Test and Guidelines for the Authentication of New-World Honeys*
2:55	H12 – **Asim Mushtaq** *Modification of chitosan for synthesis of curcumin and siRNA loaded particles for breast cancer*
3:00	H13 – **Salma Ahmed** *Synthesis of pH-sensitive nanoparticles from degradable amphiphilic di-block copolymers, utilizing RAFT polymerisation and novel chain transfer agent*
3:05	H14 – **Bruna Cambraia Garms** *Injectable and degradable hydrogel for post-surgical brain cancer treatment*
3:10	H15 – **Tania Alajo** *Influence of simulated weathering on polypropylene microplastic properties and quantitation by pyrolysis gas chromatography mass spectrometry*
3:15	H16 – **Katrina Wruck** *Activation of Heulandite type Zeolites to Synthesise Zeolite LTA*
3:20	*End of Session*
3:30	**Afternoon Tea**
4:00	**Plenary Lecture P3: Dr. Bryan Tuten – Chair: Sandra Wiedbrauk** *Exploring the Synergy between Macromolecular, Multicomponent, and Chalcogen Chemistries*
4:45	**Presentation of Prizes and Closing Remarks: Andres Reyes Zuluaga**
5:00	**The Symposium will be followed by a social gathering to stimulate further networking at the Botanical Bar**

P1. Coordination Polymers as Chiral Probes and Sensors

Carol Hua*, Hui Min Tay, Shannon Thoonen

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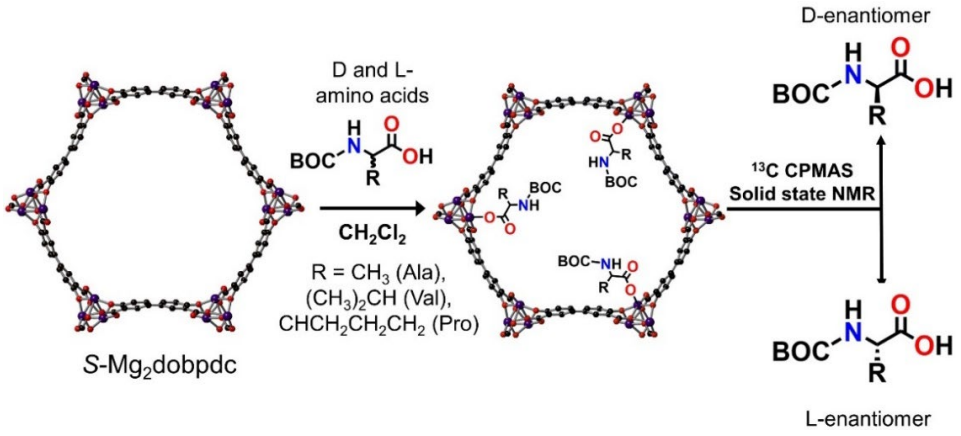
Chirality is prevalent throughout nature with most biologically important molecules being chiral, including DNA, proteins and sugars. The chirality of drug molecules is particularly important as each enantiomer may interact with metabolic and regulatory processes in vastly different ways. This is illustrated by the enantiomers of dopamine; L-dopamine is used to treat Parkinson's disease whilst D-dopamine elicits neurotoxic side effects. The development of new methods for determining the chiral purity of molecules is of great importance to the pharmaceutical, agrochemical and food industries with 56% of drugs in use consisting of chiral molecules.

Coordination polymers (CPs) and Metal-Organic Frameworks (MOFs) are crystalline materials comprising of inorganic nodes bridged by multidentate ligands to form extended structures. The high porosity and tunability of CPs enable the systematic modification of pore chemistry and size. Tailored chiral environments can be designed, making these materials well-suited to act as chiral selectors as they can encapsulate guest molecules in a manner similar to natural enzymes. The development of CPs as analytical chiral sensors and probes is attractive for determining chiral purity due to their simplicity and convenience.

This presentation will detail the synthesis of chiral CPs incorporating 1,2-*trans*-diaminocyclohexane[1] and amino acid derived ligands[2] where integral role of host-guest interactions in the application of these chiral CPs as solid state chiral sensors and probes will be highlighted. The discrimination of chirality in amino acids by ^{13}C solid state NMR using [Mg_2(*S*-dobpdc)] (dobpdc^{4-} = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate) will be discussed (Figure 1).[3]



1. H. M. Tay, C. Hua, "*Co(II) coordination polymers constructed from a bent chiral linker: controlling framework topology using co-ligands*", *CrystEngComm*, **2020**, *22*, 6690-6698.

2. H. M. Tay, C. Hua, "*Chiral Cd(II) coordination polymers based on amino acid derivatives: the effect of side chain on structure*", *Cryst. Growth Des.*, **2020**, *Cryst. Growth Des.*, ***2020**, 20, 5843-5853*.

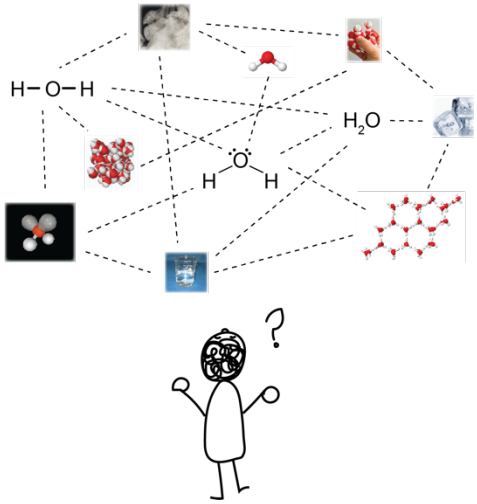
3. H. M. Tay, A. Rawal, C. Hua, "*Chiral elucidation of amino acids with S-Mg_2(dobpdc)*", *DOI: 10.1039/D0CC05539E*.

P2. Scaffolding Engagement and Capturing Student Thinking in Hybrid Learning Environments

Gwen Lawrie*

School of Chemistry & Molecular Biosciences, University of Queensland, St Lucia, Queensland 4072, Australia

Engaging students in the process of independent and active-learning within hybrid learning environments requires the careful integration of multiple instructional scaffolding strategies including formative feedback. An aim of instructional design in chemistry is to support the development of students' skills towards 'thinking like a chemist'. Expert chemists apply a constellation of representations, across multiple modes, as part of their disciplinary discourse. For tertiary chemistry teachers, the combination and subsequent function of these representations is critical to supporting student learning. A further consideration is the diversity in students' pre-existing mental models and prior knowledge, this impacts on their ability to recognize, transform, connect and construct understanding through multimodal representations. In practice, the question becomes 'Do you see what I see?'



Our research is situated within the design based research paradigm which is pragmatic, grounded, interactive, iterative, flexible, integrative and contextual[1]. I will share recent research outcomes and how these have been applied to scaffolding learning in hybrid environments in practice. Our findings indicate that student engagement with chemistry formalisms and surface features of representations can be successfully supported by careful sequencing of learning objects. Examples of student-generated representations and explanations will also be shared to illustrate strategies for the development of their representational competencies and the delivery of formative feedback in supporting student learning.

[1]Wang, F. and Hannafin, M.J. (2005), Design-based research and technology-enhanced learning environments. *Educational Technology Research and Development*, Vol. 54, pp. 5–23.

P3. Exploring the Synergy between Macromolecular, Multicomponent, and Chalcogen Chemistries

Bryan Tuten*

School of Chemistry & Molecular Biosciences, University of Queensland, St Lucia, Queensland 4072, Australia

Chalcogen chemistry and multicomponent chemistry have found widespread use throughout the field of macromolecular science. Only recently have all three of these fields been combined to create new, high chalcogen content soft matter materials. In this presentation we explore some of the recent advancements in the work of sulfur and selenium based multicomponent reactions in macromolecular science. Starting with visible light photogenerated thioaldehydes and their extreme versatility as a ligation platform in macromolecules. Further, these visible light photogenerated thioaldehydes can be harnessed in Passerini-type multicomponent polymerizations affording functional polymers with thioester moieties directly into the polymer backbone. These thioester-based soft matter materials provide a versatile functional handle for either rapid polymer degradation or polymer expansion. Finally, we take a step further down Group 16 to selenium and its ability to react as a monomer in a multicomponent polymerization in elemental form. The combination of amines, isocyanides, and elemental selenium lead to an entirely new class of polymeric materials, poly(seleno ureas). The unique spectroscopic fingerprint of selenium provides numerous different avenues into soft matter material characterization, typically impractical in standard (C-, N-, O-based) materials.

A1. Title: A novel SERS-biosensor for determination of protein biomarkers

Mahnaz D. Gholami*, Prashant Sonar, Godwin A. Ayoko, Emad L. Izake

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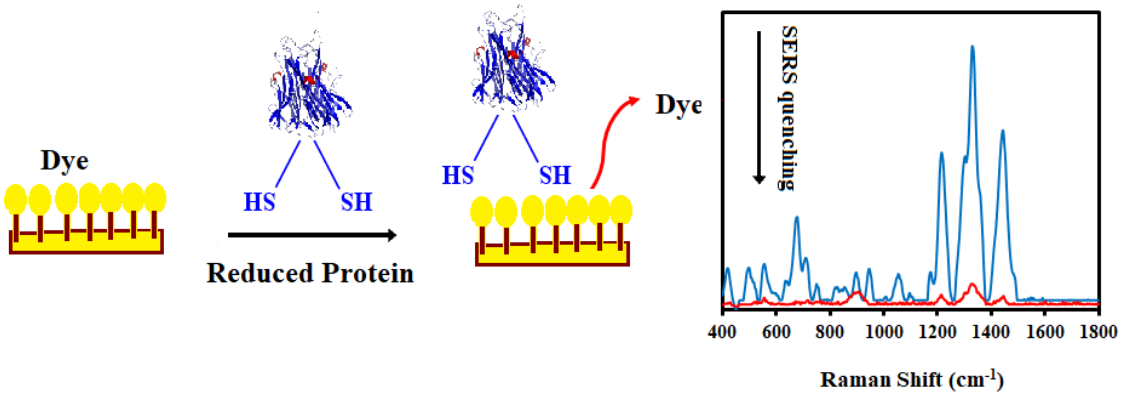
Tumour necrosis factor-α (TNF-α) is a major pro-inflammatory cytokine and responsible for broad range of physiological and pathological signalling events within cells. In this research, a facile, rapid and highly selective biosensor is developed for determination of TNF-α via Surface enhanced Raman spectroscopy (SERS). The gold coated SERS substrate was functionalised with an azo dye as a Raman probe [1]. TNF-α was extracted selectively from blood plasma by a target-specific extractor chip. The disulfide bond of TNF-α was then reduced chemically to generate free sulfhydryl (SH) terminal groups. The reduced TNF-α competes with the per-adsorbed dye on the functionalised substrate due to high affinity of the SH groups to the gold. This causes the displacement of the dye molecules from SERS functionalised substrate. The Raman signal of the dye was reduced proportionally with concentration of reduced TNF-α. Since disulfide bonds between cysteine residues are fundamental building blocks in peptides and proteins. Therefore, the new SERS biosensing method can be used for the determination of protein biomarkers.



References:

Gholami M.D., Manzhos S., Sonar P., Ayoko G, E.L Izake, (2019) Dual Chemosensor for the Rapid Detection of Mercury (II) Pollution and Biothiols. Analyst,144, 4908-4916.

A2. Optimisation of extraction procedure and LC-DAD-MS methodology for anthocyanin analysis in pigmented corn kernels.

Hung Trieu Hong*, Tim O'Hare

Centre for Nutrition and Food Sciences, Queensland Alliance for Agriculture and Food Innovation, University of Queensland, Coopers Plains, QLD 4108, Australia

Hung Trieu Hong; h.trieu@uq.edu.au

Pigmented corn is a rich source of anthocyanins, natural blue purple and red pigments that have demonstrated various potential health benefits such as antihypertensive and anti-inflammatory activities, as well as preventative activities in age-related cognitive decline and memory loss. Several studies have attempted to extract and quantify the anthocyanins of pigmented corn. However, low stability of anthocyanins following extraction and a strong tendency for anthocyanins to remain bound to the corn matrix are still major issues to be addressed. This study used internal standards of delphinidin-3-glucoside to validate the efficiency of extraction procedure together with optimisation of the liquid extraction procedure for anthocyanins. An ultra-high performance liquid chromatography–diode array detector-mass spectrometry (UHPLC-DAD-MS) method was developed for characterisation and quantification of anthocyanin components in the complex corn matrix. The anthocyanin profiles and total anthocyanin content (TAC) of mature seeds of pigmented corn were reported. A total of eighteen anthocyanins, mainly cyanidin-, peonidin-, and pelargonidin-based glucosides, were identified and quantified. Cyanidin-based glucosides were the major pigments of purple-pericarp sweetcorn (75.5% of TAC) and blue-aleurone maize (91.6%), while pelargonidin-base glucosides composed the main anthocyanins of reddish-purple-pericarp sweetcorn (61.1%) and cherry-aleurone maize (74.6%). Importantly, it could be clearly demonstrated that previously reported acetylated and succinylated anthocyanins in corn kernels are generated during the extraction process and are not genuine corn pigments. These findings are crucial to providing a correct anthocyanin profile of pigmented corns, and emphasize the importance of using acidification during the extraction process for corn-based anthocyanins, and potentially other anthocyanin-containing commodities.

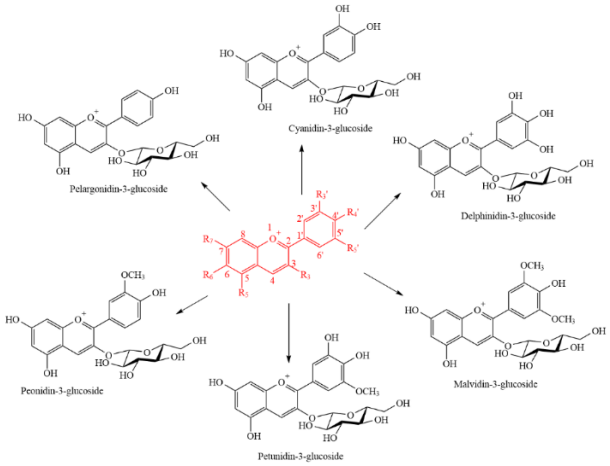


Figure 1: Molecular structures of the six most common anthocyanins in plant-based foods.

A3. Calculation methods for Cellulose Crystallinity Index using X-ray Diffraction

Tony Wang[12]*

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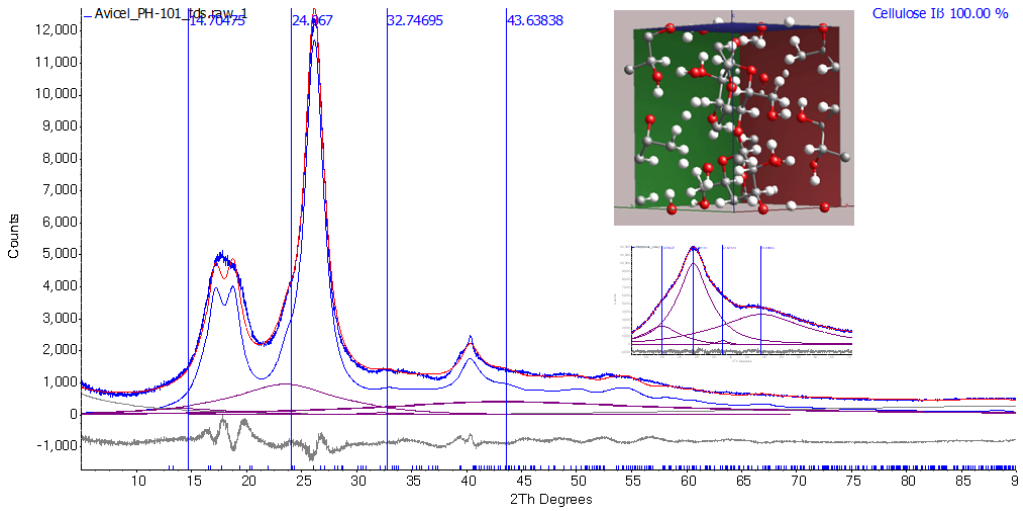
The physical and chemical properties of cellulose depend on its crystallinity, i.e. how well parts of the long chain molecule aligns with each other. An important indicator to describe the periodicity of cellulose molecule chain arrangement is called Crystallinity Index (CI), which is commonly measured using X-ray Powder Diffraction. There have been many calculation methods [1,2] of CI used in literature, which usually only allow relative evaluation of CI in a batch of samples. Some of the methods depends on optics and slits width used during measurement, which limit the CI comparison between research reports, while other methods suffer model correlations hence unstable. These methods are applied to a cellulose standard Avicel PH-101 and compared in this study. The proposed CI calculation method in this research uses additional information, including the crystal structure of the crystalline part and the measured diffraction profile of the amorphous part from ball-milling, which largely overcomes above model correlation problem.



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A4. Application of an ICPMS method to determine nineteen clinical trace elements concentrations in whole blood and plasma: investigation of the effect of storage temperature

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Assessing the concentrations of trace elements in blood contributes to our evaluation of health status, and assists in the prediction and treatment of certain disease states or deficiencies and occupational exposures. A simple alkaline dilution ICP-MS method was developed with full laboratory validation, in accord with ISO 17025:2017, for the rapid and high-throughput routine analysis of nineteen trace and ultra-trace elements in small volumes of blood samples (0.1 mL). The developed method was applied for the accurate quantification of nutritionally essential elements: cobalt, copper, iodine, molybdenum, zinc, manganese and selenium; the nutritionally probably-essential elements: chromium, vanadium, nickel, and bromine; and non-essential or toxic elements including lead, cadmium, mercury, arsenic, bismuth, antimony, thallium and uranium in blood and plasma samples from adult population samples in Queensland. The method was also applied to investigate the effects of freezing and refrigeration on the concentrations of trace elements in blood and plasma samples stored at three different temperatures (4°C, -20°C and -80°C) over a one-year period at multiple time points. Significant differences ($p < 0.0001$) were observed between blood and plasma concentrations of six essential elements: cobalt, copper, manganese, molybdenum, selenium and zinc. Whole blood concentrations of these trace elements were significantly correlated with plasma concentrations. The distribution of the trace elements between human blood and plasma varied considerably for the different elements. The results also indicate that sample storage in freezer and ultra-freezer are more effective preservation methods for the ICPMS analysis of trace elements.

Acknowledgements:

The authors acknowledge Australian Red Cross LifeBlood for their generous provision of blood samples and blood materials.

A5. The characterisation of novel precursor compounds for the production of illicit drugs by isotope ratio mass spectrometry

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Isotope ratio mass spectrometry (IRMS) is used to measure stable isotope profiles of illicit drugs and precursor compounds. Presented is a survey of the stable isotope profiles of traditional and novel precursors for the illicit drugs 3,4-methylenedioxyamphetamine (MDA) and 3,4-methylenedioxymethylamphetamine (MDMA) commonly known as 'ecstasy'. The control of traditional precursors safrole, isosafrole, piperonal and 3,4-methylenedioxyphenyl-2-propanone (MDP2P) has seen the clandestine synthesis of MDA and MDMA from uncontrolled 'novel' alternative compounds.

Significant variation in isotopic compositions were found across the surveyed precursors, especially for novel precursors, suggesting that stable isotope profiling may be used to compare and differentiate precursors used in the production of MDA and MDMA. IRMS may also be used to group or discriminate MDA and MDMA synthesised from these precursors.

Also presented is an investigation into isotopic fractionation during the hydrochloride salt precipitation of MDMA. Results show that no fractionation is observed in carbon or oxygen stable isotopes. However, when multiple precipitations were required to collect all MDMA, isotopic fractionation was observed in hydrogen and nitrogen. These results have implications when comparing isotopic compositions between batches of MDMA.

A6. Agarose Encapsulated Vitamin B12a Coated Gold Nanoparticle Aggregates for pH modulated SERS Based Detection of Cyanides, Sulphur Dioxide & NO_x Gases

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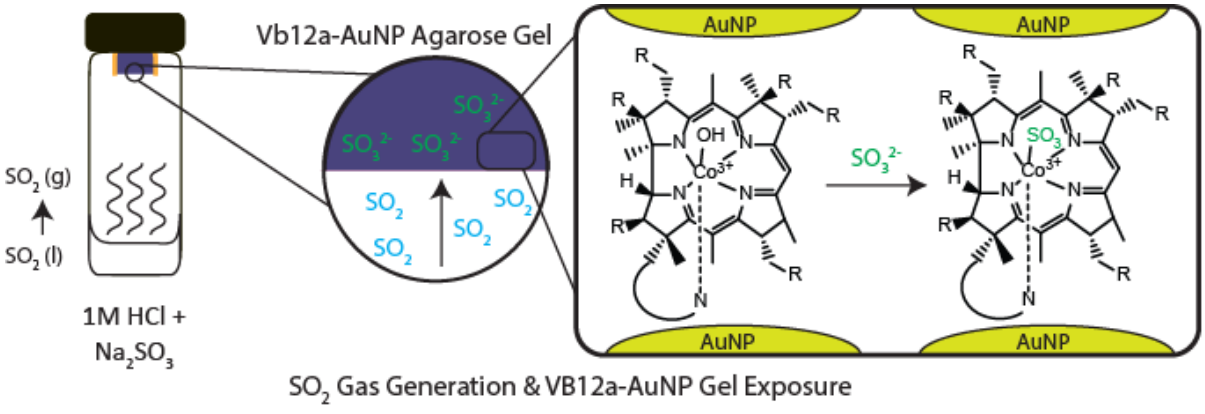
Surface Enhanced Raman Spectroscopy (SERS) is a highly promising molecular sensing technique, especially in aqueous and biological applications due to high sensitivity, rich spectroscopic information and excellent water compatibility. A noble metal substrate is required to achieve SERS and gold nanoparticle (AuNP) aggregates can provide large enhancements. However, these aggregates will undergo agglomeration and sedimentation with time, which can be prevented through incorporation into a polymer hydrogel substrate,[1] or slowed down by coating the particles with suitable molecular stabilises.[2] Direct SERS based sensing with AuNPs can have issues with complex mixtures and weak Raman signals which can be overcome with the incorporation of a reactive probe such as a cobalamin (Vitamin B12a) that then targets the desired analyte – resulting in highly sensitive, selective SERS detection with potential for a ratiometric response.

Vitamin B12a and related compounds (cobalamins) have a heavily investigated rich chemistry and here we show they also have a novel application as a reactive probe in an AuNP based SERS sensing system for the detection of hydrogen cyanide, sulphur dioxide and NO_X gases. By first coating AuNPs with hydoxocobalamin (VB12a), followed by aggregation in order to generate high SERS enhancements and then trapping these aggregates in an agarose hydrogel matrix, we successfully demonstrate that this pH tuneable system can give a ratiometric SERS signals for the detection of multiple toxic gases. Simultaneous detection of these gases at the same time may also be achieved, with the pH of the hydrogels influencing how sensitive the anions are to each target molecule.



SO_2 Gas Generation & VB12a-AuNP Gel Exposure

Figure 1: Generation and detection of sulphur dioxide gas utilising VB12a-AuNP Agarose Gels

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A7. A Plasmonic recyclable nickel foam sensor for the therapeutic drug monitoring of Meropenem in blood by SERS

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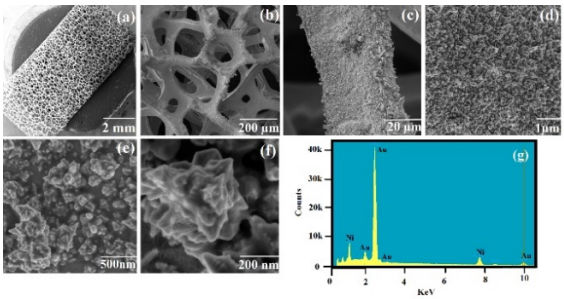
A rapid and sensitive plasmonic nickel-based nanomaterial was developed for the therapeutic drug monitoring of Meropenem (a carbapenem antibiotic) using surface enhanced Raman spectroscopy (SERS). The gold nanostructures were deposited on the nickel foam using chronoamperometric method which led to a high enhancement factor of 1.6×10^{11}. The SEM-EDX analysis confirm the morphology and chemical composition of the deposited nanostructures. The new nanomaterial was developed to directly quantify and monitor Meropenem in human blood plasma and LOQ was determined as 1 pM. The sensor was also used in HPLC-SERS assembly to demonstrate selectivity and to provide fingerprint identification of Meropenem in human blood plasma. Moreover, the SERS measurements were reproducible in aqueous solution and human blood plasma (RSD = 5.5 %) and (RSD = 2.86 %) respectively at 200 µg/mL (n= 3) and successfully recycled using a simple method and hence, used for the repeated determination of the drug by SERS. Therefore, the new sensor has a strong potential to be applied for the therapeutic drug monitoring of Meropenem at points of care and intensive care unit.



Reference: Muneer, S., Sarfo, D. K., Ayoko, G. A., Islam, N., & Izake, E. L. (2020). Gold-Deposited Nickel Foam as Recyclable Plasmonic Sensor for Therapeutic Drug Monitoring in Blood by Surface-Enhanced Raman Spectroscopy. *Nanomaterials*, *10*(9), 1756.

A8. Development and Application of Method to Analyse the Sialylation of the cells

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Sialyltransferases (STs) catalyse the transfer of sialic acids (sias) to the cell surface and hence participate in key biophysiological processes in human health and diseases, such as cancer. Therefore, ST is a potent therapeutic target in anti-cancer drug development. However, there are currently no cost-effective ST inhibitor screening assays readily available to measure the effectiveness of proposed inhibitors. This project, therefore, aimed to develop a simple method to determine sias in cells to evaluate the extent of sialylation caused by proposed ST inhibitors.

The most common type of sia in human, N-5-acetylneuraminic acid (Neu5Ac), was successfully detected and quantified via a reverse phase HPLC with triisopropanolamine buffer solution as the ion-pairing reagent. The proposed method resulted in the successful separation of Neu5Ac with the retention time of 6.344min at 0.4mL/min. The method was validated according to the AOAC guideline: R^2=0.999, LOD=0.002487mM, LOQ=0.007537mM, average recovery of 102% from spiking, with 1.99% and 9.44% of average inter-day and intra-day precision.

From the developed method, deoxycholic acid (DOC) – a known ST inhibitor, was added to the HeLa cells to evaluate the extent of sialylation inhibited by DOC against the control (no DOC added). As depicted in Figure 1, the proposed method was able to evaluate the extent that DOC changed the sialylation of the cells, as Neu5Ac level decreased significantly as the concentration of DOC increased.

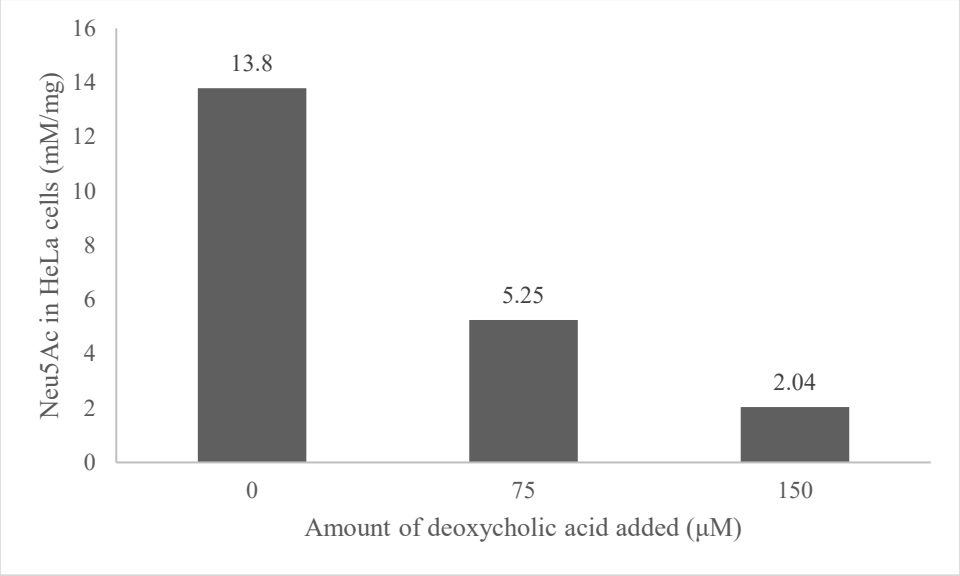

Figure 1. *The changes in Neu5Ac level in Hela cells according to various concentrations of deoxycholic acid (0 µM), 75 µM and 150 µM). The values are mean±SD, n=3. The asterisks indicate the Neu5Ac level for 75 µM and 150 µM was statistically significantly different to the control: * P < 0.05; **P < 0.001.*

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A9. Identification of volatile plant compounds in *Pimelea trichostachya* responsible for livestock aversion

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Pimelea poisoning of cattle is unique to Australia and caused by native *Pimelea* species due to the inadvertent consumption of dry *Pimelea* plants growing amongst other pasture plants. The toxin responsible for the poisoning has been identified as the novel diterpenoid orthoester simplexin. Green *Pimelea* plants give off a strong unpleasant odour and are reported to be generally avoided by grazing cattle. This odour is considered the reason cattle avoid green *Pimelea* plants and is hypothesised to be a terpene or terpenoid which is potentially biosynthetically related to simplexin. To date, there are no reports on the characterisation of the *Pimelea* plant volatiles. This study aims to identify the volatiles responsible for the odour causing cattle aversion towards *Pimelea* plants. Volatile compounds of the *Pimelea* species, *P. trichostachya* were sampled by static headspace solid-phase microextraction (SPME) method using a SPME manual holder fitted with polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fiber. Volatiles were analysed by GC/MS using a Shimadzu GC-2010 Plus gas chromatograph coupled to a Shimadzu GCMS TQ8040 mass spectrometer. Compounds that were detected were identified by spectral library (NIST) comparisons. Results to date have identified plant metabolites including hydrocarbons, terpenes and fatty acids which were matched to the spectral library with at least 90% similarity. Some plant volatiles matched with the library were further confirmed by co-elution with reference standards where available. Future studies will include analysis of plant material extracted in solvent to look for less volatile "simplexin-like" compounds and the identification of volatile plant compounds in other *Pimelea* species, *P. elongata* and *P. simplex*.

A10. Manipulating redox-active supramolecular complexes by mass spectrometry

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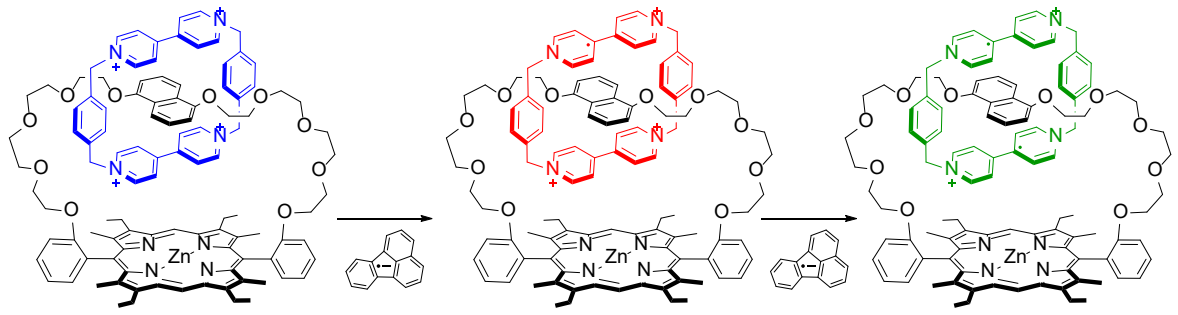
Mechanically interlocked complexes such as rotaxanes and catenanes are attractive candidates for molecular machinery, capable of responding to external stimuli such as oxidation and reduction. Crystallography and NMR are gold standard methods that are heavily relied upon to determine stoichiometry and discriminate competing molecular topologies but require relatively large amounts of purified material.

Here we present gas-phase electrochemical reduction in an ion trap mass spectrometer as a dual-function tool to synthesise and probe the reactivity of interlocked bipyridinium-based complexes with macrocyclic crown ethers. Electrospray ionisation transports the complexes into the mass spectrometer intact, where a high-resolution mass analyser provides a rapid confirmation of stoichiometry, but no structural insight. Even in complex mixtures, tandem mass spectrometry (MS/MS) enables the analyst to isolate and interrogate individual complexes in order to examine the energetics and reactivity of the complex and probe the inter-connectivity of the molecular constituents.

The gas-phase reaction of multiply charged bipyridine-based complex cations with an anionic reducing agent yields intact complexes in lower oxidation states, despite the strong exothermicity of the ion-ion recombination reaction.
Pure populations of radical intermediates are easily accessible in high yield, even on compounds that have not been specially purified or crystallised. We demonstrate that electron-rich macrocyclic porphyrin ethers retard electron transfer reaction rates, compared with non-complexed archetypes.[1] We propose that relative electron transfer reaction rates can be considered as a useful proxy for gas-phase reduction potentials.



[1] D. L. Marshall, B. L. J. Poad, E.T. Luis, R. A. Da Silva Rodrigues, S. J. Blanksby, K. M. Mullen, *Chem. Commun.* **2020**, *56*, 13575-13578

B1. Structure activity relationship study of ketol-acid reductoisomerase inhibitor NSC116565

Julia L. Kurz*, Xin Lin, Khushboo M. Patel, Shu Jie Wun, Waleed Hussein, Nick West, Gerhard Schenk, Luke W. Guddat, Ross P. McGeary

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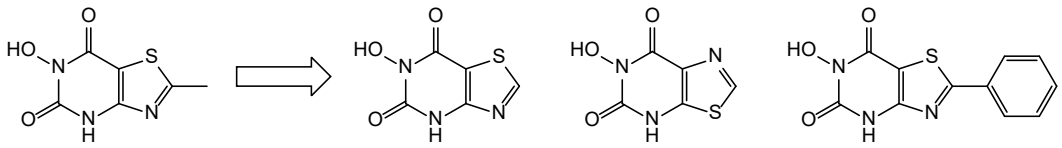
Tuberculosis (TB) is an infectious disease which poses a significant threat to global human health. TB is so problematic due to the development of multi-drug resistant strains. Therefore, there is an urgent need to develop new TB drugs. Ketol-acid reductoisomerase (KARI) is a metallo-enzyme present in bacteria which is involved in the synthesis of branched chain amino acids. This pathway is vital for bacterial survival, yet not present in animals, allowing potent inhibitors of KARI to be toxic to bacteria without impacting the human host. Recently, a novel inhibitor of *M. tuberculosis* (*Mt*) KARI, NSC116565 (see below), was discovered. This compound inhibits *Mt* KARI at nanomolar concentrations. Crystal structures of NSC116565 bound to *S. aureus* KARI (98% active site homology with *Mt* KARI) have been obtained and show that this compound is able to bind to both the open and closed conformations of the enzyme. Promisingly, NSC116565 kills virulent *Mt* cells at low micromolar concentrations. Structure activity relationship studies have been carried out where the methyl group of NSC116565 has been replaced with other substituents. In addition, isomers where the position of the sulfur and nitrogen within the thiazole are switched have been synthesised.



NSC116565

B2. Structure–Activity Analysis of A Self-Adjuvanting Cyclic Multicomponent Lipopeptide Delivery System for Group A *Streptococcus* Peptide Antigens

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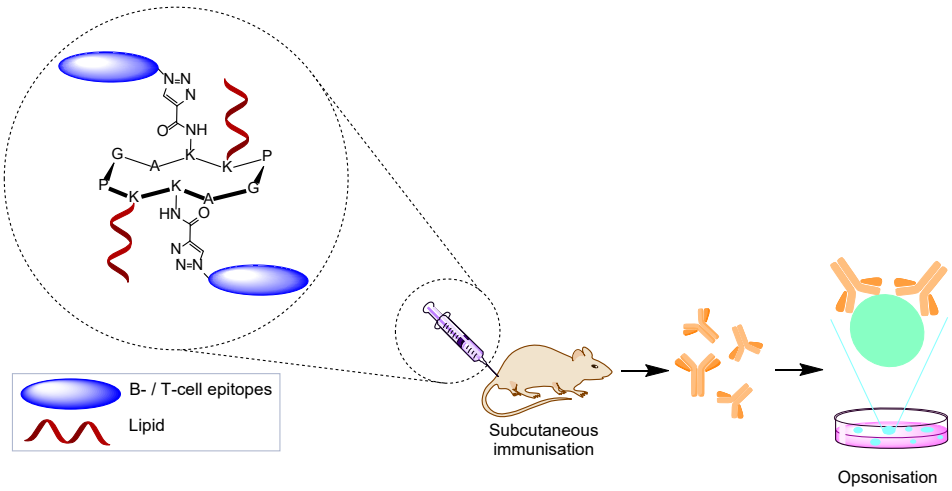
Infection with Group A *Streptococcus* (GAS) can cause a wide range of diseases, from minor throat infections to serious life-threatening invasive infections such as necrotising fasciitis. GAS is also the principle etiologic agent of rheumatic fever and rheumatic heart disease, which are responsible for the largest proportion of the over 320,000 GAS related deaths worldwide per year.[1] The ever-present global burden of GAS and the large number of cases, which manifest to rheumatic heart disease, highlight the need for a safe and effective vaccine. Here, we have investigated a cyclic decapeptide carrier incorporating a conserved B-cell peptide epitope derived from the conserved region of the GAS M protein, a universal T-helper epitope and a synthetic toll-like receptor 2 targeting lipid moiety as a possible self-adjuvanting GAS vaccine.

A structure-activity relationship analysis of the vaccine candidate showed successful induction of GAS-specific IgG when administered subcutaneously without an additional adjuvant, with all lipidated vaccine candidates inducing antibody titres significantly higher than the negative control. Interestingly, a physical mixture of the vaccine components (instead of a conjugated vaccine) showed the highest antibody titres of all vaccine groups. Further, vaccine-generated antibodies were shown to effectively opsonise multiple strains of GAS bacteria.[2] This proof-of concept study showed the capability for a self-adjuvanting cyclic delivery system to act as a vehicle for the delivery of GAS peptide antigens to treat GAS infection. Results from this study provide a vaccine delivery system capable of inducing high titres of opsonic antibodies capable of opsonising several clinically significant strains of GAS bacteria.



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B3. Analysis of Approaches to Anti-tuberculosis Compounds

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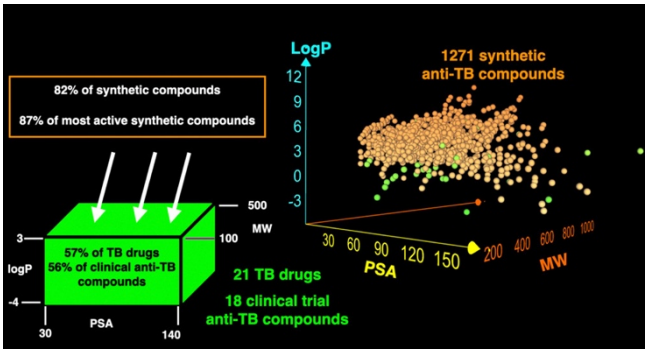
Mycobacterium tuberculosis (Mtb) remains a deadly pathogen two decades after the announcement of tuberculosis (TB) as a global health emergency by the World Health Organization. Medicinal chemistry efforts to synthesise potential drugs to shorten TB treatments have not always been successful. Thousands of compounds have been synthesised by medicinal chemists with the aim of TB inhibition; however, only a small percentage of these compounds has shown appropriate potency. Here, we analyse physiochemical properties of 39 TB drugs and 1271 synthetic compounds reported in 40 publications from 2006 to early 2020. We also propose a new TB space of physiochemical properties that may provide more appropriate guidelines for design of anti-TB drugs.



Reference:

Motamen, S.; Quinn, R. J. Analysis of Approaches to Anti-tuberculosis Compounds. *ACS Omega*. **2020**, *5*, 28529-28540.

B4. Exploring the potential of endophytes and fungi as sources of antimicrobial compounds

Jianying Han[1], Xueting Liu[2], Lixin Zhang[2], Ronald J Quinn[1], Yunjiang Feng[1]

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Microorganisms are one of the most important resources for providing prolific active natural products and drug leads, including clinically used drugs such as streptomycin, cycloserine, kanamycin, caperomycin and rifampicin. Here,

1) Genome- and MS-based mining methods were used to study the secondary metabolites of the phytopathogenic fungus *Bipolaris sorokiniana* strain 11134. Forty-six biosynthetic gene clusters were predicted, including PKS, NRPS, and TPS. Chlorinated chromones and meroterpenoids were identified and the antibacterial activity was evaluated.

2) Bioassay guided isolation was also used for chemical study of active endophytic and fungal extracts. High throughput screening against *M. smegmatis* gave 21 fungal and 7 endophytic extracts out of a total of 350 extracts with MIC value less than 400 μg/mL. Fifty compounds have been isolated, including 9 active compounds.

3) Based on both the activity data and chemical analysis, nine active strains were selected for co-cultivation to mimic the natural ecological situation. Preliminary results showed that the chemical profile of 17 out of 218 co-cultured extracts significantly changed during the interaction. These biological data and chemical profiles lay the foundation for all further potential new compounds study.

B5. Application of polyethylenimine as an intranasal adjuvant for intranasal group A *Streptococcus* vaccine

Charles C. Dai [1,*], Jieru Yang[1], Waleed M. Hussein[1], Lili Zhao[1], Xiumin Wang[1], Zeinab G. Khalil[2], Robert J. Capon[2], Istvan Toth[1,2,3] and Rachel J. Stephenson[1]

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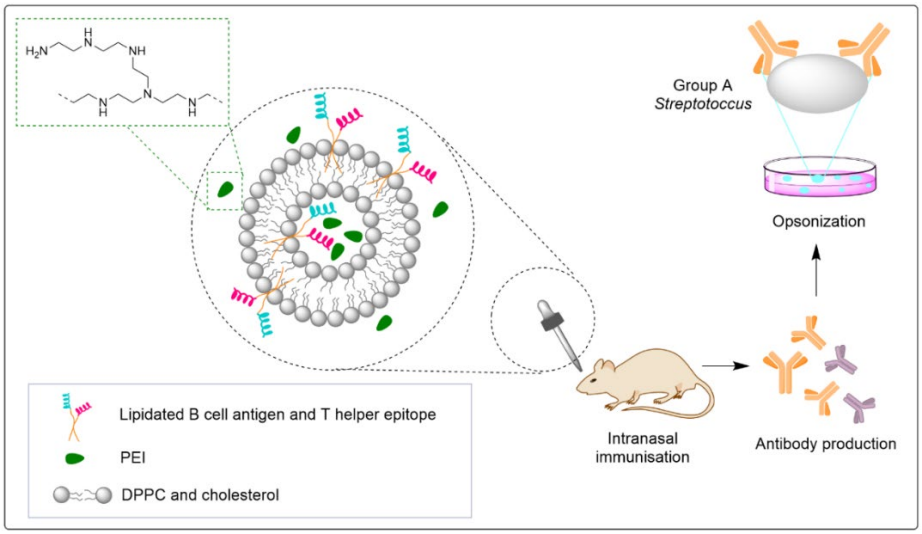
Group A *Streptococcus* (GAS) and its related diseases are global challenges, and they affect 34 million people worldwide with more than 345,000 deaths annually.[1] However, there is currently no commercial or licensed GAS vaccines available. Vaccines have many routes of administration, including subcutaneous and intramuscular injection, or intranasal and oral delivery. Here, intranasal delivery has many benefits, including decreased needle-free and non-invasive administration and induction of the systemic and mucosal immunity inducing a rapid local and protective immune response.[2]

Polyethylenimine (PEI) is a hydrophilic cationic polymer, and PEI-coated nanoparticles, used as drug delivery systems, have been shown to promote the cellular uptake and improve the immune responses.[3-5] In this study, we successfully demonstrated the development of PEI incorporated liposomes for the delivery of a lipopeptide-based vaccine against GAS. Outbred mice were administrated with the vaccine formulations intranasally with three boosts, and immunological investigation showed the PEI liposomes elicited both significant mucosal and systemic immunities with the production of IgA and IgG antibodies. Antibodies were shown to effectively opsonise multiple isolates of clinically isolated GAS from Australia. This proof-of-concept study showed the capability for PEI liposomes to act as a safe vehicle for the delivery of GAS peptide antigens to elicit immune responses against GAS infection, making PEI a promising addition to liposomal mucosal vaccines.



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B6. Interrupting the Conversation: *In Silico* Design of Dual Acting Quorum Quenching Agents

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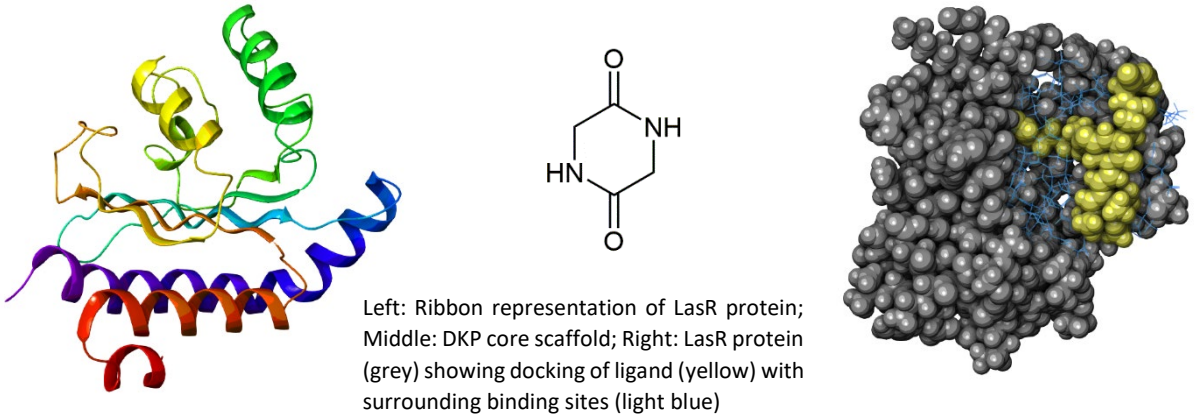
Bacteria communicate via a process known as Quorum Sensing (QS). This phenomenon allows bacteria to adapt to their surrounding environment and survive harsh conditions such as pH changes, nutrient deficiencies and antimicrobials such an antibiotics.[1] One of the ways in which bacteria can survive these conditions is by forming a biofilm. Biofilms are an aggregation of planktonic cells coated in an Extracellular Polymeric Substance (EPS) which form on surfaces and interfaces and are resistant to antibiotics.

Previously, our group has shown that a class of stable free-radical compounds called nitroxides are able to disperse biofilms back into planktonic cells, which are more susceptible to antibiotics.[2] Additionally, there has been much work in the literature around synthetic quorum quenching agents being used to control the quorum sensing systems of bacteria. In this work, we used *in silico* modelling to design dual-action anti-biofilm compounds, based on the highly modifiable diketopiperazine scaffold. These compounds, containing both a nitroxide moiety and common motifs from known QS molecules, were designed to dock into the LasR protein. This protein sits at the top of the quorum sensing hierarchy of *Pseudomonas aeruginosa* and as such, presents an important therapeutic target.[3]



Left: Ribbon representation of LasR protein; Middle: DKP core scaffold; Right: LasR protein (grey) showing docking of ligand (yellow) with surrounding binding sites (light blue)

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B7. Identification of Potential Chemical Probes from *Macleaya cordata* (Willd) R. Br.

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Phenotypic screening of a library of traditional Chinese medicinal plant extracts against a human olfactory neuroshpere-derived (hONS) cell line gave indications that the ethanolic extract of *Macleaya cordata* elicited strong perturbations to various cellular components. Further chemical investigation of this extract resulted in the isolation of two new benzo[*c*]phenanthridine alkaloids, (6*R*)-10-methoxybocconoline (**1**) and 6-(1-hydroxyethyl)-10-methoxy-5,6-dihydrochelerythrine (**2**). Their planar structures were elucidated by extensive spectroscopic studies. The absolute configuration of **1** and relative configuration of **2** were assigned by density functional theory (DFT) calculations of ECD and NMR data, respectively. Also isolated were fourteen known metabolites, including ten alkaloids (**3**–**12**) and four coumaroyl-containing compounds (**13**–**16**). Phenotypic profiling of the isolates against Parkinson's Disease (PD) patient-derived olfactory cells revealed bocconoline (**3**) and 6-(1-hydroxyethyl)-5,6-dihydrochelerythrine (**4**) significantly perturbated the features of cellular organelles including early endosomes, mitochondria and autophagosomes. Given that hONS cells from PD patients model some functional aspects of the disease, the results suggested that these phenotypic profiles may have a role in the mechanisms underlying PD and signified the efficacy of CP in finding potential chemical tools to study the biological pathways in PD.

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Nguyen, D. T.; Iqbal, J.; Han, J.; Pierens, G. K.; Wood, S. A.; Mellick, G. D.; Feng, Y., Chemical constituents from *Macleaya cordata* (Willd) R. Br. and their phenotypic functions against a Parkinson's disease patient-derived cell line. *Bioorganic & Medicinal Chemistry* **2020**, *28* (21), 115732.

B8. In-silico family-wide profiling of the poly (ADP-ribose) polymerase superfamily.

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The poly (ADP-ribose) polymerase (PARP) superfamily has generated much attention in recent years due to their involvement in cancer and airway pathologies. To date, only inhibitors of PARP1-3 are clinically approved. The limitation in the development of new inhibitors has been in achieving selectivity due to the highly conserved catalytic domain. We analysed the catalytic domain, WWE domain, and the macrodomains of the PARP superfamily using an *in-silico* profiling protocol. X-ray crystal structures were obtained from the protein data bank and homology models were generated using SWISS-Model for the PARP enzymes without an X-ray crystal structure. Protein-Protein Basic Local Alignment Search Tool was used to validate and compare structure similarity and UCSF Chimera was used to perform 2D and 3D protein alignment and structural analysis with MatchMaker tool and Clustal Omega alignment tool. Across the catalytic domains, PARP10's residues were the least conserved with at least six unique residues identified in and adjacent to the binding pocket. In contrast, most other PARPs, only had 1-3 unique residues with PARP12 being the most conserved. The WWE domains showed no conserved residues and of the macrodomains, macro-2 displayed a high level of divergence in the amino acid sequencing although they all displayed a conserved protein fold. The macro-3's binding pocket, when compared to macro-2, was superficial and hydrophilic whereas macro-2 displayed a buried and hydrophobic pocket. In summary, we have identified the residues that are unique and conserved across the PARP superfamily in hope to lead the next generation of drug discovery.

B9. Selecting orange *Capsicum* as a source of dietary zeaxanthin

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Capsicum species consist of both chillies and sweet/bell-shaped capsicums. The vibrant colours of capsicums are associated with carotenoids, some of which have positive effects on human health. Carotenoids like zeaxanthin and lutein have been associated with slowing the progression of Age-related Macular Degeneration (AMD). AMD is one of the leading causes of blindness in elderly people in developed countries such as Australia. Past studies have indicated that orange-coloured capsicums are a good source of zeaxanthin, however there is a dearth of information regarding orange capsicum varieties in the Australian market. The present study focuses on profiling both orange chillies and orange capsicums available in Australia, and to identify those varieties that could be used as a rich source of zeaxanthin. Five orange chillies and eight orange sweet-capsicum varieties were investigated for their carotenoid profiles by UHPLC-DAD-ESI-MS. Seven of the eight orange capsicums had zeaxanthin as their principal carotenoid, however one orange capsicum, which had a darker orange hue, had violaxanthin and capsanthin (yellow and red colour carotenoid pigments, respectively) as its principal carotenoids. Similarly, three (*C. annuum*) of the five chillies demonstrated capsanthin (diluted concentration) as their principal carotenoid, while 'Bulgarian' (*C. annuum*) had violaxanthin and lutein as the principal carotenoids, and Peruvian chilli ('Aji Amarillo', *C. baccatum*) principal carotenoids consisted of zeaxanthin, α-carotene and β-carotene. The present results suggest that orange colour of different *Capsicum* varieties can be due to zeaxanthin or a mixture of carotenoids, and therefore colour should not be the only determinant for selecting high zeaxanthin lines.

B10. Design and synthesis of rhamonosyl glycotope to protect against *streptococcus pyogenes*

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Introduction: S. pyogenes is a widespread primary infective agent in humans and causes ~700 million human infections each year, beginning from mild streptococcal pharyngitis (strep throat) to invasive streptococcal pneumonia, necrotizing fasciitis, toxic shock syndrome, and myositis [1]. In addition to causing post-streptococcal sequelae, such as rheumatic heart disease (RHD), rheumatic fever (RF) and acute glomerulonephritis. The estimated total economic burden of GAS-induced disease in Australia, according to 2015 birth rates, was more than 44 million AUD with GAS-induced heart diseases, RF and RHD contributed more than 16 million AUD [2, 3]. Carbohydrate-based vaccines have been proven to be the most promising subunit vaccine candidates, as the bacterial glycan pattern are different from that of the mammalian cells and show more conservancy amongst pathogen serotypes than that of the protein components. In this work, we implemented the outcomes of the recent contributions of reverse vaccinology to develop a glycan-based subunit vaccine against *S. pyogenes*. We adapted a facile method for the synthesis of the glycotopes of *S. pyogenes* to be later conjugated to self-adjuvanting lipo-peptide and cyclic peptides.

Methods: We have adapted a robust method to prepare the glycotope of *S. pyogenes* which is a blend of liquid-phase and solid-phase glycan synthesis requiring a single orthogonally protected rhamnosyl monomer (Figure 1).

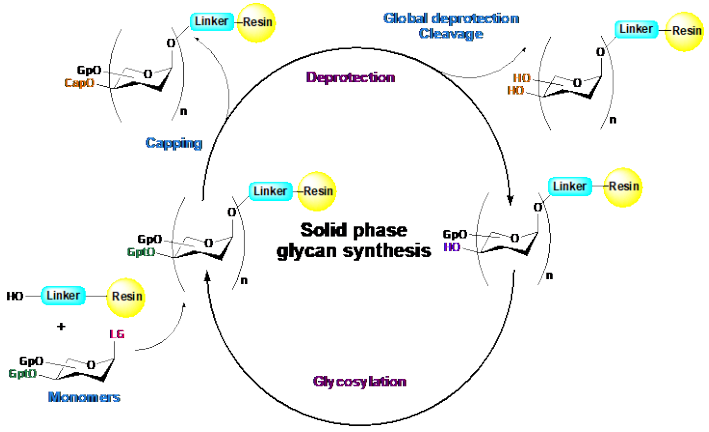

Figure 1: Solid phase glycan synthesis and automated glycan assembly

Results: Orthogonally protected rhamnosyl monomer building blocks have been successfully prepared and the structure have been confirmed by NMR and mass spectrometry analysis. The scheme for glycotope synthesis via solid-phase glycan synthesis will also be presented.

Acknowledgements: Researcher supported by Funding from the National Health and Medical Research Council, Australia (Grant numbers: APP1037304 and APP1158748) and the University of Queensland, Australia.

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B11. Deciphering selectivity and divergent responses in boronolectin fluorophores

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In the field of glycobiology nothing is more valuable than the detection and quantification of glycans, both on cell surfaces and in serum. Commercially available lectins are primarily targeted towards quantifying medically relevant glycans like glucose and sialic acid (Neu5Ac). These are often based off naturally occurring proteins; however, in the last 20 years a new type of lectin has been proposed called boronolectins. Boronolectins exploit the reversible covalent bonds that occur between boronic acids and alcohol groups. Whilst synthesising a library of such synthetic lectins, some were found to have unique fluorescent responses. Our previous molecule published in 2009 showed specificity for Neu5Ac and a unique divergent response dependant on which of the two boronic acids was bound.[1] In more recent years, we have found a second molecule with divergent response, this time differentiating between glucose and galactose through changing fluorescent intensity.

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B12. Intranasal Vaccination with a Lipopeptide-anchored Liposomes Vaccine Candidates against Streptococcus Pyogenes

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Many researchers have made efforts to create effective vaccines against Group A Streptococcus. Most of the vaccine studies has focused on the subunit vaccines based on M protein. However, the application of whole protein as a vaccine antigen can lead to autoimmune reactions. Consequently, epitopes derived from M protein have been utilized as safer alternatives to classical vaccine. Here, we have selected J8 peptide that is derived from GAS M-protein and P25 peptide as B cell and T cell epitopes, respectively. Nonetheless, these epitopes could not induce strong immune responses on their own. To overcome this drawback, these epitopes have been attached to surface membrane of liposome by a lipid moiety. This work aims to examine the influence of special arrangement of cholesterol- antigen conjugates in liposomal formulation on immunogenicity.

Synthesis of the vaccine candidates was carried out by Fmoc SPPS method. Anchoring of the lipopeptides to a liposome was performed using a film hydration method. Characterization of lipopeptide-anchored liposome by DLS and TEM was performed. Determination of the liposome stability was also studied over 6 months. Furthermore, the ability of compounds to induce humoral immunogenicity was evaluated in mice.

The particle sizes of four liposomes were similar (less than 200 nm), while the charges were different (20-40mV). All formulations produced spherical particles as confirmed by TEM. The sizes of all liposomes were stable for the period of 6 months, with minimal fluctuation in the size distributions. The highest antibody titers (IgG) were induced in mice vaccinated with (Ac-J8-K(CH)-P25+ liposome).

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C1. Applying Molecular Networking to Natural Products Chemistry

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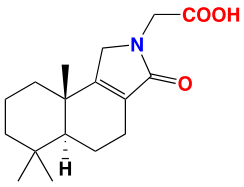
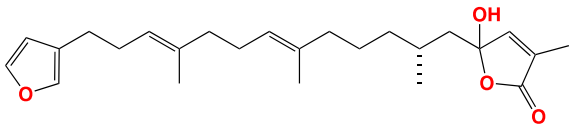
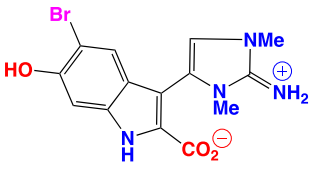
Advancements in analytical, chemical and spectroscopic technologies, and rapid and robust dereplication and prioritization methodology, have greatly enabled the discovery of new natural products (NPs) from complex natural extracts. This thesis reviews these advances and seeks to apply best practice to explore a library of ~1,000 southern Australian and Antarctic marine sponges, algae and tunicates. In particular, this thesis explores the application of advanced mass spectroscopy (UPLC-QTOF-MS/MS) and Global Natural Products Social Molecular Networking (GNPS) guided prioritization. GNPS molecular network guided search of extract library successfully detected three southern Australian marine sponges, as sources of three new classes of compounds. Detailed chemical analysis of a *Dysidea* sp. extract led to isolation of dysidealactams A–F (**1.1**–**1.6**) and dysidealactones A–B (**1.7**–**1.8**); a *Cacospongia* sp. extract led to isolation of cacolides A-L (**2.1**–**2.12**) and cacolic acids A-C (**2.13**–**2.15**); and a *Thorectandra* sp. extract led to isolation of a novel compound, thorectandrin A. Additionally, this molecular network effectively identified a *Geodia* sp. sponge as a new source of a rare class of indolo-imidazole alkaloids, trachycladindoles. Further chemical analysis of this sponge extract led to the isolation of the new trachycladindoles H–M (**3.8**–**3.13**). In addition to expanding knowledge of marine natural products, this study demonstrates the value of applying GNPS molecular networking to map chemical diversity and prioritize the selection of marine sponge extracts for more detailed chemical analysis.



dysidealactam A (**1.1**)



cacolides A (**2.1**)



trachycladindole H (**3.8**)

C2. How wastewater analysis be used as a tool to measure the population treated pain burden?

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Wastewater analysis is able to quantify multiple pharmaceutical compounds in order to estimate consumption in the population, an approach known as wastewater-based epidemiology (WBE). Pain is a global health priority, the assessment of which is challenging. Here we propose a new concept of estimating the population burden of treated pain using wastewater analysis. Wastewater samples collected from areas representing whole communities and the consumption of drugs used to treat pain - nonsteroidal anti-inflammatory drugs (NSAIDs) and opioids can be measured. By the systematic collection of wastewater followed instrumental analysis, the total consumption rate of NSAIDs or opioids within a population group can be measured. By combining consumption estimates utilizing DDD or morphine equivalents, the community burden of treated pain can be estimated by assessing the number of causes with mild to moderate pain for NSAID and strong to severe pain for opioids. We propose this method can be used to evaluate the treated pain burden in population between locations and over time. In the future, WBE can be evaluated as a tool to measure community pain burden via consumption estimates that shows promise in describing spatial and temporal trends in population treated pain burden.

C3. Release of Plastics to Australian Land from Biosolids End-Use

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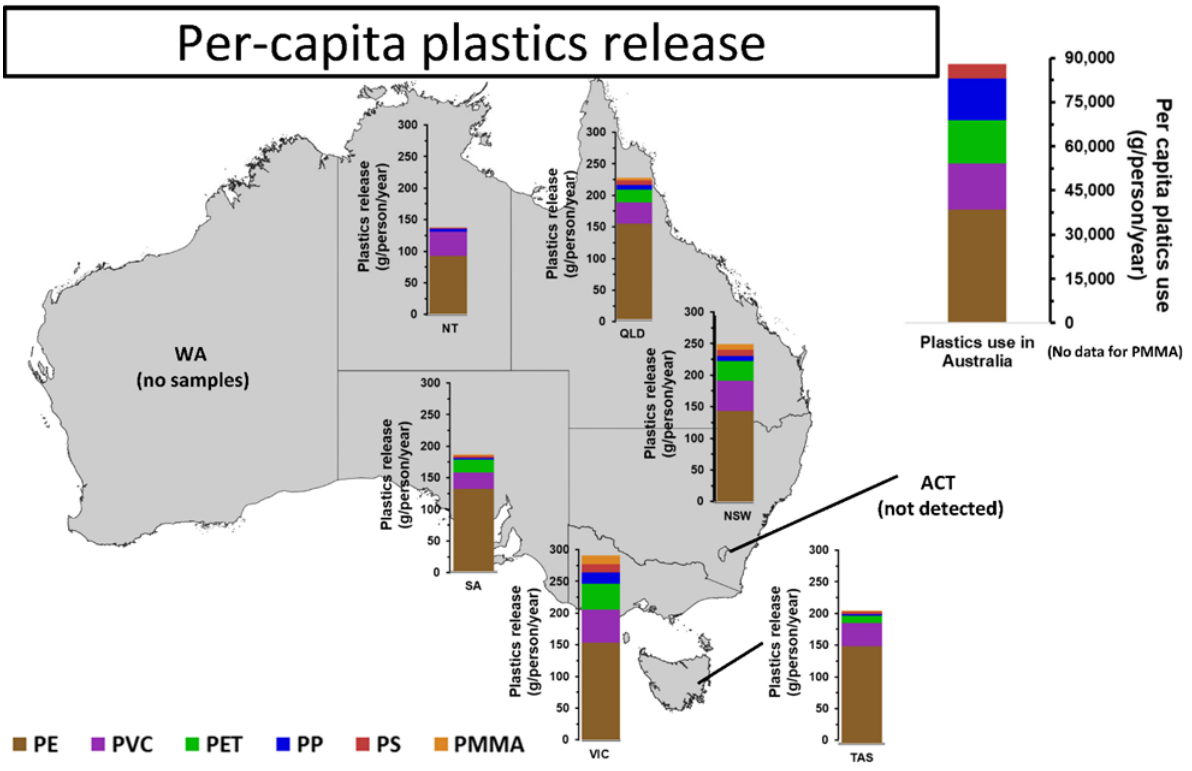
Plastics are contaminants of emerging concern that can enter the environment from multiple sources, including via land application of treated sewage sludge (biosolids). Biosolids samples collected from 82 wastewater treatment plants across Australia and covering 34% of the population during census week in 2016 were quantitatively analysed to estimate the release of seven common plastics. Quantitative analysis was performed by pressurized liquid extraction followed by double-shot micro furnace pyrolysis coupled to gas chromatography mass spectrometry. Ninety nine percent of the samples contained plastics (Σ_6Plastics) at concentrations of between 0.4 and 23.5 mg/g dry weight (median; 10.4 mg/g dry weight) while polycarbonate was not detected in any sample. Per-capita mass loads of plastics (Σ_6Plastics) released were between 8 and 877 g/person/year across all investigated wastewater treatment plants. Polyethylene was the predominant plastic detected, contributing to 69% of Σ_6Plastics. Based on the concentrations measured, it was projected that around 4,700 metric tons (Mt) of plastics are released into the Australian environment through biosolids end-use each year, equating to approximately 200 g/person/year, which represents 0.13% of total plastics use in Australia. Of this, 3,700 Mt of plastics are released to agricultural land and 140 Mt to landscape topsoil. Our results provide a first quantitative per-capita mass loads and emission estimate of plastic types through biosolids end-use.



C4. Development and validation of a method for metformin and oxypurinol in wastewater samples

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Gout and diabetes are growing global health issues lead to potential chronic conditions such as obesity, hypertension and heart diseases. Monitoring prevalence of diabetes and gout could be effective in prevention of these two diseases and evaluate public health policies. Analysing human metabolites of diabetes and gout related pharmaceuticals in wastewater provides high temporal/spatial resolution of public health information of diabetes and gout. Due to the hydrophilic of compounds in aqueous environment, current analysis using liquid chromatography-tandem mass spectrometry (LC-MS/MS) while compounds are not retained with retention time with the hold-up time. The study aims to develop a simple and rapid LC-MS/MS method using HILIC column in simultaneous determination of metformin and oxypurinol in wastewater. Different types of LC columns (C8, C18, HILIC) were used based in direct injection mode. Using HILIC column (ACQUITY UPLC BEH Amide Column, 1.7 µm, 2.1 mm X 100 mm) showed a good retention of compounds and samples were simply diluted before instrument analysis. The optimised method was successfully applied in wastewater samples collected from Australian census day's samples.

C5. Discovery of New Pyranonaphthoquinones from an Australian Terrestrial Bacterium CMB-PB42

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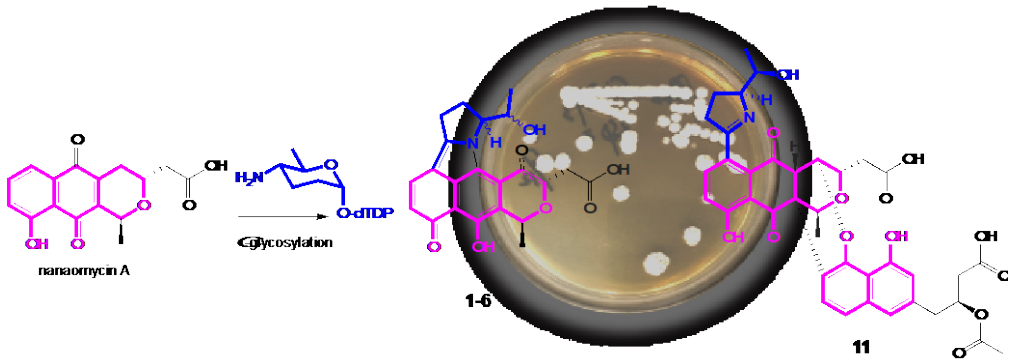
Abstract: Pyranonaphthoquinones are a distinct subclass of aromatic type II polyketides, prominently produced by the soil-dwelling bacterial species of the genus *Streptomyces*.[1] Many of them have been documented to display a diverse array of interesting biological activity, including antibacterial, antifungal, antiviral and anticancer properties.[2] The basic structure of the pyranonaphthoquinones is the naphtho[2,3-c]pyran-5,10-dione ring system. Natural pyranonaphthoquinones usually vary in the substitution of the pyran and aromatic rings, and can possess additional fused ring systems, such as a γ-lactone to the dihydropyran moiety, whilst in others the lactone is ring-opened to the carboxylic acid side chain.[3] As part of our ongoing investigation on novel and bioactive secondary metabolites from Australian terrestrial microbes, we isolated a rare class of pyranonaphthoquinones, **1-9, 11** and **12**, with intriguing rearranged deoxyaminosugar moiety fused to the naphthoquinone ring system from the EtOAc extract of the culture plates of a soil-derived bacterial CMB-PB42. Another cometabolite **10** was found to be the precursor of the dimeric **11** and **12**. Herein, we describe the spectroscopic and chemical analysis leading to the structural elucidation for **1-12** with commentary on a plausible biosynthetic relationship.



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C6. Investigation into the Chemical Transformation of Enterocin from Australian Soil Derived *Streptomyces spp*.

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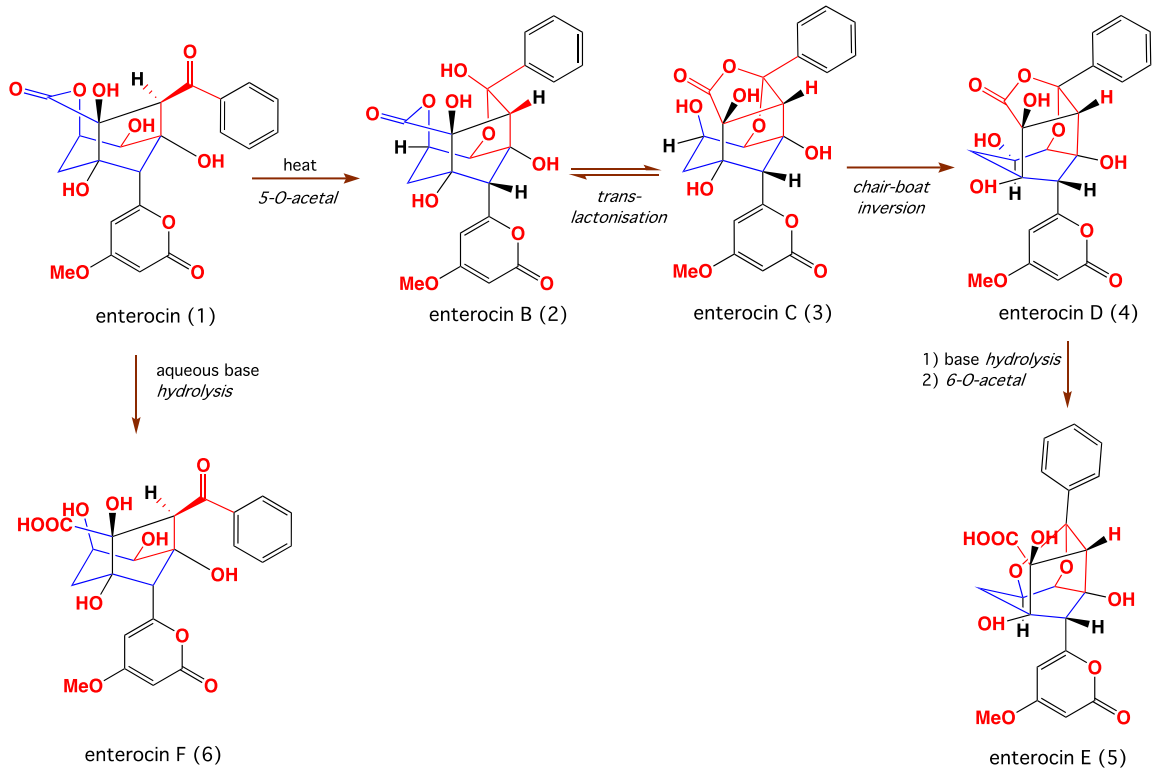
Chemical analysis of cultivation of an Australian soil derived *Streptomyces* spp. CMB-MRB492 was found to produce enterocin (**1**), a known biologically active compound along with two new analogues, enterocin B (**2**) and C (**3**).[1-4] Further investigation revealed that the polyketide enterocin **1** is responsive to environmental stimuli and transformed into the isomeric acetal enterocins B and C under mild heating condition; which existed in equilibrium through intramolecular trans lactonization. Enterocin C subsequently undergo pseudo-chair−boat inversion to the more stable enterocin D (**4**) in room temperature. Stable under neutral and acidic conditions, enterocin D transforms into acetal enterocin E **(5)** under aqueous basic conditions. Enterocin **(1)**, when exposed to aqueous base, is converted to the isomeric Michael acceptor enterocin F **(6)**. The conversion of enterocin into enterocin B and C was suppressed in acidic conditions even during heating conditions. The structures of enterocin analogues (**1-4**) were assigned by NMR spectroscopic analysis and absolute configuration based on the reported configuration of enterocin. Enterocins A–D did not exhibit significant growth inhibitory activity against a selection of Gram-positive and -negative bacteria. The study describes a possible transformation pathway of enterocin under different environmental stimuli and demonstrates that the knowledge of environmental stimuli and associated artifacts is critical to understanding the chemical and ecological properties of enterocins and other classes of natural products.[5]



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C7. Resource Recovery from Acid Mine Drainage

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With the current trend of depletion of natural resources, attention has been made on the area of waste recovery of valuable metals. With Acid Mine Drainage (AMD) being of great environmental concern, recovering valuable metals from the waste stream is beneficial. This ultimately can allow for a cost-effective method of treating the waste product, be profitable for the mine and alleviate the environmental impact of the waste storage. The focus of this research will be on the synthesis of high purity alumina from AMD and the synthesis of calcium sulphate dihydrate (gypsum) both via the lime neutralisation process. The approach of recovering both products was a combination of common hydrometallurgical processes including lime precipitation, acid leaching and crystallisation. The AMD (pH 3.72) was neutralised to pH 6.5 and 8.5, both extremes of the ANZECC guidelines to determine what impact if any the neutralisation played on the overall purity of the product. The neutralisation product was then leached with cold (0ºC) 20% HCl solution, with the digest solution being sparged with anhydrous HCl chloride to precipitate aluminium chloride hexahydrate (ACH). The ACH product was redissolved in deionised water and recrystalised twice to improve the purity of the product with the final ACH being thermally decomposed at 1200ºC to produce alpha alumina with a purity of 99.99 wt%. The solid residue from the acid digestion was washed with 20% HCl followed by deionised water until a neutral pH of the supernatant was achieved. This resulted in the gypsum being of 99.9% purity.

C8. Chemical digestion methods: what are the real impacts on microplastics?

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Field collection and laboratory-controlled exposure studies are critical to establishing the toxicity and long-term consequences of aquatic plastic debris and their associated chemical contaminants (e.g. plasticisers) on organisms. A critical aspect of these studies relates to the separation and retrieval of plastics from biological sample matrices using a variety of extraction techniques. Popular separation methods for micro and nano-size plastics involve prolonged, high temperature treatment using a range of alkali, oxidative and/or acidic chemical reagents (e.g. 60^{o}C with nitric acid). While these techniques offer a more efficient and robust means of sample clarification, their strongly acidic and oxidative properties have been associated with enhanced polymer reactivity and plastic fragment deterioration. Considering many identification and characterisation techniques utilised by marine scientists post-recovery involve qualitative visual assessment and comparative spectroscopy, it is imperative that the chemical and physical characteristics of the plastic polymers are not impacted during chemical digestion. Here, we apply an analytical approach to characterise and quantify the reactivity and degradative impacts of common chemical digestion methods on polystyrene-based microplastics, chosen because of their high prevalence in aquatic environmental globally. Based on these results, chemical digestion methods will be ranked to determine their appropriateness for microplastic separation, and recommendations for updates to future protocols will be offered.

C9. Characterising weathered microplastics to better understand their sorption behaviour in the environment

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Microplastics are now found throughout the natural world, raising concern about their potential environmental impacts. In the environment microplastics undergo physical and chemical weathering processes that transform their surfaces. This has potential implications for environmental behaviour and so their impact. Yet despite this, relatively little research has focused on microplastic surface characteristics, compared to properties such as polymer type. The aim of this project is to understand how microplastic surface characteristics, changed by environmentally relevant conditions can impact their sorption behaviour. We tested the hypothesis, that due to an increase in surface roughness, area and oxidation, there will be an increased rate in chemical uptake via sorption with weathering. Microplastic nurdles of varying polymer types (high and low density polyethylene, polypropylene, polystyrene) are being exposed to a xenon arc lamp weathering chamber, set to replicate natural sunlight conditions, then characterised for their surface characteristics. Fourier-transform infrared spectroscopy (FTIR) will be used to measure oxidation state of the microplastic surface, atomic force microscopy (AFM) for surface roughness and Brunauer–Emmett–Teller (BET) surface analysis for surface area. This will be followed by a subsequent measurement of sorption rate over time, of model protein bovine serum albumin (BSA) onto the microplastic material, to analyse for changes in sorption behaviour with change in microplastic characteristics. Current progress will be presented, to highlight the significance of specific surface characteristics in defining environmental behaviour and impact.

C10. Isolation of new microbial natural products using Global Natural Product Social (GNPS) molecular networking approach

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Natural Products (NPs) have been a major source for many drug leads for the treatment of different infectious and non-infectious diseases. They provide distinct array of complex molecules that can act as new drug leads.[1] Modern NPs research encounters challenges as continuous re-discovery of known microbes and known metabolites.[2] Therefore, there is a huge demand to develop fast and reliable dereplication techniques to resolve the complexity of the crude extracts. Global Natural Products Social (GNPS) molecular networking (MN) is an innovative technique that can visualize large data sets by assembling them into groups (clusters) depending on the similarity of the MS/MS fragmentation spectra.[3] This technique provides rapid dereplication of the known chemical entities, allow the rapid identification of new chemical scaffolds and identify new from known metabolites in a very the complex crude data sets. In addition, it identifies related analogues of known compounds providing variable dereplication ability.[4]

In this study, we employed a detailed chemical investigation for microbial crude extracts isolated from >100 microbial strains that were isolated from different sources such as, Australian termite nest, mangrove associated plants and soil, mullet fish gut. Through GNPS molecular networking, we were able to prioritize interesting fungi strains (x 4) isolated from unexplored resources. One fungus (CMB-TN39F) isolated from termite nest, two from mangrove microbes (CMB-MB018, CMB-LS015F) and one from mullet fish gut (CMB-F661). These 4 fungi were subjected to large scale cultivation followed by isolation and chemical characterization to yield an array of chemically and structurally different new metabolites.

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C11. Bioactive Natural Product Prioritization in Venomous Animals Microbial Collections Using Multi-informational Feature-based Molecular Networks

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The current challenge in the field of microbial natural products lies in developing strategies to prevent the rediscovery of known chemistry in addition to discovery of biologically-relevant molecules. The advent of the Global Natural Social Molecular Networking (GNPS) platform has made it possible for mass spectrometry data to be used for compound dereplication even in a very complex crude extract. The platform also makes it possible to take into account other information that can be used for compound prioritisation such as biological activity. In this study, MSMS data of the microbial crude extracts from venomous animals such as centipedes, cone snails, spiders, snakes, scorpions, and wasps were used to generate a feature-based molecular network (FBMN) through the use of GNPS platform. Antibacterial activity (against *Staphylococcus aureus*), taxonomical, and source organism data were integrated to the molecular network to prioritise microbial strains to undergo further investigation. Priority strain CMB-SN005B was subjected to chromatographic techniques (SPE, Prep HPLC) in order to isolate predicted bioactive nodes. The isolated compounds were then tested against methicillin-resistant *Staphylococcus aureus* and vancomycin-resistant *Enterococcus faecalis* strains.

C12. A study of PFOA destruction using Combined Ultrasonication (US) and Advanced Oxidation Processes (AOP) involving Ozone (O_3) - (US/O_3 system).

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Development of an effective water treatment methodology for Poly- and perfluoroalkyl substances (PFASs) is highly challenging due to their unique physical and chemicals properties, and extremely low health and environmental regulatory standards are established due to toxicological effects, bioaccumulation and high persistence.

Although, conventional water treatment processes are ineffective for PFAS, there are some effective techniques, could only separate PFASs either from liquid to solid phase or concentrate. Their inability to eliminate PFASs from the environment is a major drawback. However, advanced destruction techniques involve high cost due to high energy use, high capital and/or operational costs. Despite the laboratory scale experiments are promising for PFASs remediation, large-scale field applications have limitations due to various unknown PFASs and precursors with unique properties and varying water quality parameters.

This laboratory bench scale study was conducted in a 500 mL glass beaker, using Branson Digital Sonifier with frequency between 19.85-20.05 kHz. Comparison study was carried out only using Ultrasonication (US) and US/O_3 system with 1, 10 and 100 mg/L PFOA solutions in laboratory deionised water. The results suggest, there is a 5% degradation of 10 mg/L PFOA in 2h ultra sonication, based on fluoride concentration using Dionex Ion Chromatograph (ICS-2000), as a measure to PFOA degradation. No apparent variation in PFOA destruction between US only and US/O_3 systems was identified. However, further studies are recommended in making firm conclusions with system optimisation.

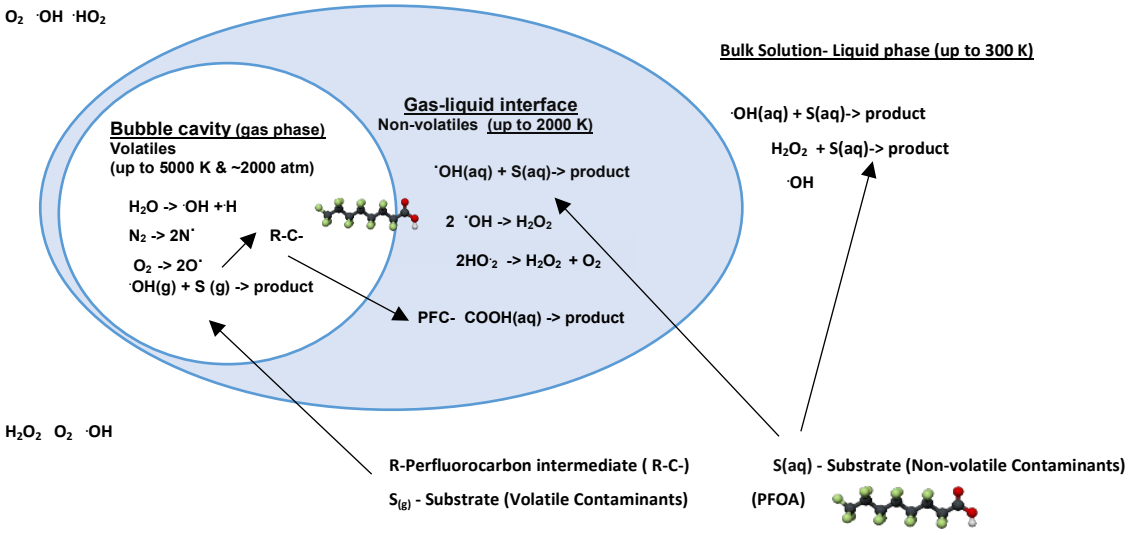

Figure 1: Conceptual model of reactions in three zones of ultrasonic cavitation bubble

Source: (Adopted from, "Jurate Virkutyte and Ekaterina V. Rokhina (2010), Figure 9.1 (p.324) in Jurate Virkutyte, Rajender S. Varma and Veeriah Jegatheesan, Treatment of Micropollutants in Water and Wastewater, ISBN: 9781843393160, © IWA Publishing".) With permission

Source:https://en.wikipedia.org/wiki/Perfluorooctanoic_acid#/media/File:PFOA-3D.png

Acknowledgement:

I wish to thankful to Dr Les Bowtell for his involvement as a supervisor to this research project.

D1. Photocatalytic benzyl alcohol oxidation using facet controlled ZnO nanocatalysts

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Zinc oxide materials are interesting because their physical and chemical properties can promote high-performance as functional materials for various applications. ZnO has a wide band gap (3.37 eV) with a high binding energy of 60 meV. ZnO is a cheap material and its ability to govern organic redox reactions at room temperature conditions endows promising advantages over other conventional catalysts. Therefore, exploring ZnO semiconductor as a catalyst for synthetic organic reactions is a significant important research direction in the field of sustainable organic synthesis reactions. In this study, cone-shaped ZnO nanocrystals with exposed reactive oxygen terminated {10$\bar{1}$1} facets, rod-shaped ZnO nanocrystals where {10$\bar{1}$0} facets are predominantly exposed and plate shape ZnO where {10$\bar{1}$1} and {0001} exposed were synthesized using a non-hydrolytic aminolysis synthesis route. The nanoparticles were characterized by TEM, BET, XPS, XRD and Uv-Vis. The 3 different shaped ZnO nanocrystals were tested for Friedel crafts acylation of aromatic compounds to investigate its catalytic properties. Reaction products and conversions were analysed using GC and GC-MS. Having different facets exposed in different shapes of ZnO catalysts exhibited, different reaction rates with different product selectivity for methoxybenzophenone. Among them ZnO nanocones gave the highest starting material conversion. To investigate the materials' photocatalytic behaviour, ZnO were used as a catalyst for benzyl alcohol oxidation. Benzaldehyde was obtained as the product with 100% selectivity in every shape tested. Different reaction conversions of benzyl alcohol oxidation were resulted due to different band structure and surface adsorption properties of ZnO nanocones, nanorods and nanoplates.

D2. Photo-switchable product selectivity control in Aniline based synthesis

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One of the greatest challenges in chemistry is to satisfy the requirement of technologies and chemical syntheses with green energy sources. Sunlight stands out as the most promising choice in this struggle with its potential for driving clean and efficient chemical transformations. Imines and sulfides are very versatile components in the synthesis of pharmaceuticals and other biologically active molecules. In this study, we have developed a novel and efficient photo promoted system to facilitate direct synthesis of imines from benzylamines using a simple organic molecule, 2,6-dimethylbenzenethiol under ambient conditions. This clean and mild synthesis method was further extended to investigate the possibility of the formation of cross coupled imines between benzylamine and aniline and has been successful. More interestingly, we were able to switch the selectivity for the products from homo-coupling to cross-coupling upon utilization of 1:1.5 of benzylamine to aniline reactant ratio under blue light irradiation. Following this discovery, we also explored the feasibility of a photocatalytic reaction pathway to couple thiophenol and aryl iodide to give diaryl sulfides using Cu as a potential element in the photocatalyst. We observed that Cu nanoparticles of 40-50 nm size range have the potential to catalyse the formation of diaryl sulfide cross-coupling product photocatalytically upon shining with visible light while the homo coupling disulfide product was observed as the major product under dark conditions. Thus, the utilization of light as a photo-switch to tune the selectivity between the homo-coupling and cross-coupling products has been successfully achieved.

D3. Multi-Material 3D Microstructures with advanced Stimuli-responsive Properties

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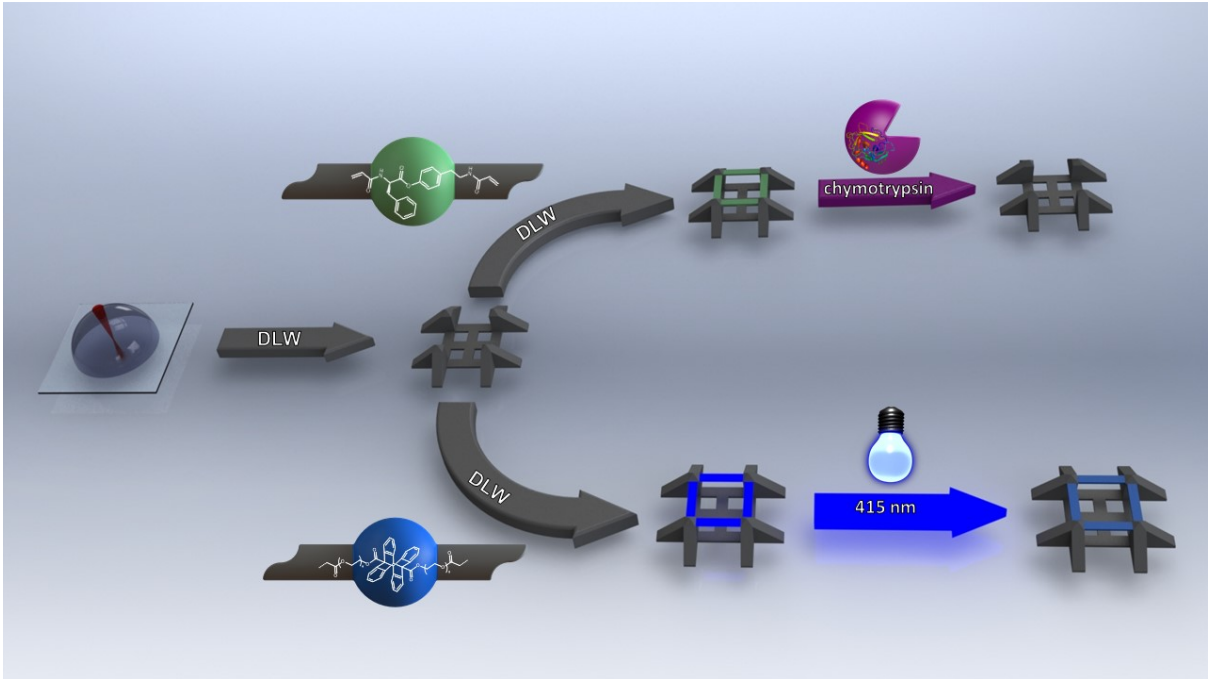
Additive manufacturing is continuing to be adopted across a wide variety of academic fields and industries and is continuing to improve in terms of sophistication. The additive manufacturing technique direct laser writing (DLW), also known as two-photon laser lithography, is on the forefront of this development, as it allows fabrication of truly three-dimensional structures on the microscopic level. One active field of research that is striving to push this technology forward is the development of advanced photoresists that are capable of fabricating structures with stimuli-responsive properties, thus imparting novel functionalities onto them. In the current lecture, two examples of such photoresists exploiting bespoke functional crosslinkers that lead to multi-material microstructures with new functionalities are presented. The first example of microstructures possesses mechanical properties that can be adjusted post-manufacturing via irradiation with visible light. The second example entails structures that can be completely degraded upon exposure to the enzyme chymotrypsin. Both types of microstructures may in the future be used to fabricate cell scaffolds in order to study the reaction of cells to these changes and represent powerful unions of molecular design and materials science.



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D4. Fully Periodic Constant Potential Simulations of Electric Double Layers

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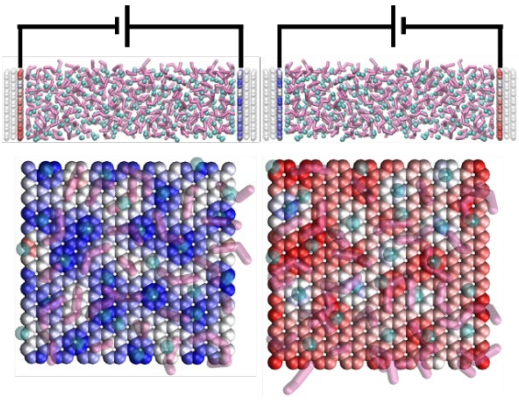
The development of better batteries and supercapacitors, for advancing technology and addressing climate change, requires better understanding of the electrode-electrolyte interface. Theoretical models of electrolyte layering near interfaces are still in their infancy, while many molecular models neglect electrode conductivity in using fixed, uniform atomic charges. In this talk I describe the constant-potential method (CPM), which dynamically updates electrode atomic charges to reflect the polarization of a conductive electrode, and its open-source implementation in the popular molecular dynamics package LAMMPS. CPM molecular dynamics enables the rigorous study of electric double layers near a charged surface, allowing the observation of phenomena such as voltage-dependent electrolyte ordering as well as the calculation of capacitance. Recent advances[1,2] also enable the application of CPM to fully periodic representations of the electrochemical unit cell, further reducing the computational cost of CPM-enabled simulations, and I will present benchmarks of the performance improvements obtained in LAMMPS.



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D5. Theoretical Understanding of Electrocatalytic Hydrogen Production Performance of One-Dimensional Metal−Organic Frameworks

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The exploration of low-cost, abundant and efficient electrocatalysts for hydrogen evolution reaction (HER) is a perquisite for large-scale hydrogen fuel generation and metal−organic frameworks (MOFs) have been recently proposed as promising electrocatalysts for the HER. To this end, a series of seven one-dimensional (1D) first-row transition metal (TM)-dithiolene MOFs with the effect of electrolyte is studied with density functional theory (DFT) calculations. Using the Gibbs free energy of the adsorption of hydrogen atoms as a key descriptor, our theoretical results find two promising candidates, Cr/Ni-based 1D dithiolene MOFs. According to the calculated electronic properties and magnetic moments of TM cations in 1D TM-dithiolene MOFs, it further reveals the existence of the $[TM^{3+}(L^{2-})(L^{2-})]^{-}\leftrightarrow[TM^{2+}(L^{\bullet-})(L^{2-})]^{-}$ electronic resonance structures in Cr/Ni-based MOFs, which is ascribed to the half and fully occupied four 3d valence orbitals of Cr^{2+} and Ni^{2+}, respectively. These electronic configurations with half and fully occupied valence orbitals can stabilize the state with more feature of S radicals, which is beneficial to the electrocatalytic HER based on the CHE model. This theoretical work enables us to elucidate the essence of improved electrocatalytic HER performance on 1D TM-dithiolene MOFs based on the resonant charge-transfer mechanism.

D6. Finite-size effects on the diffusion coefficients from molecular dynamics in crystal-like structures

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Solid-state electrolytes are important material for electrical energy storage systems. Because of that, there has been an increase on the use of computational simulations to describe these materials. Transport properties, such as ionic conductivity and diffusivity, when measured through molecular dynamics (MD) simulations, are known to be influenced by the size of the simulation box. In this work, we investigate finite-size effects on the diffusion coefficients in solid-state electrolytes from MD simulations. For that, we consider a simplified description of the system of interest, where we have a body-centred cubic lattice structure being composed of two different particles. They lighter particles are able to diffuse within the crystalline structure and their self-diffusion coefficients are analysed. When exploring the dependence of the self-diffusion coefficients with the size of the simulation box we observe very different behaviours. For example, Systems containing no vacancies on the crystalline structure present a linear dependency of the diffusivity with the inverse of the length of the simulation box, while the systems containing vacancies do not present such dependency.

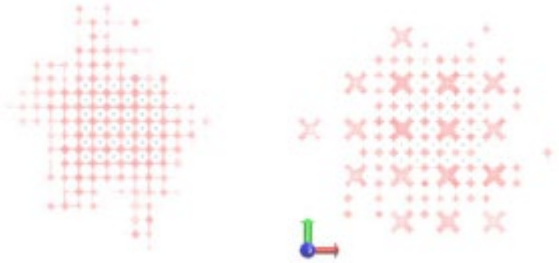

Figure 1 – Trajectory of the lighter particles on the system with no vacancies (left) and with 3.7% of vacancies (right).

D7. Sonocatalytic Degradation/Conversion of Azo Dyes to Graphene Quantum Dots Using Liquid Metal Galinstan.

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Synthetic dyes have become part of human life since its accidental discovery by William Henry Perkin in 1856 till date, and these chemicals are widely used in textile, pharmaceutical, food, paint and printing industries. However, dye wastewater disposal poses a significant environmental and socio-economic challenge to human existence, and aquatic life considering their non-biodegradable, persistent, carcinogenic, toxic and mutagenic nature. Diverse techniques have been investigated at the reduction/control of these harmful substances before their discharge. Meanwhile, azo dyes are known to be recalcitrant to conventional aerobic (biological) process, and commonly used physical/chemical treatment methods are neither cost-effective nor ecofriendly. Some of the traditional techniques explored for dye wastewater treatment include ion exchange, adsorption, absorption, ultra/nanofiltration, photocatalysis and advanced oxidation processes. The degradation/decolourization of organic dyes has been well documented using various techniques, yet some of these techniques are not practically feasible in industrial wastewater treatment plants. In the case of biological treatment using fungi and aerobic bacterial decolourization, it has been proven that only a few bacteria can effectively decolourize azo dye and enzyme production is unreliable in fungi-based decolourization of azo dyes. Besides, the toxicity of dyes is directly linked to its degradation products, which could vary mainly depending on the treatment applied. Hence, there is a need for innovative remediation approach in dye degradation to attain net-zero discharge and economic viability either by utilization of the dye or conversion to intermediate compounds. In the open literature, very few reports are available on organic dye degradation to useful compounds, though, there are thousands of essays on dye degradation and detoxification. However, the long term and immediate toxic impact of dye degradation products on living organisms are not fully understood but has been demonstrated to pose a risk.[1]

The exploration of post-transition metal alloys which includes field's metal, rose's metal, wood's metal and non-toxic room-temperature gallium-based metals in the field of wastewater treatment is relatively new. Among these metal alloys, liquid metals (gallium-based metal alloys) has recently attracted considerable attention due to its excellent electrical and thermal conductivity, reactivity with other materials, and tunable surface chemistry, etc. Moreover, the oxide passivation of liquid metals (LM) has offered additional functionalities, and the modification of this layer with other materials (metals and non-metals) have shown great potential for catalysis. Hence, its catalytic application in the field of environmental remediation could be attained using LMs for organic dye degradation/detoxification.[2] Herein, we investigated the degradation of azo dyes via ultrasonication to useful intermediate product using neutral/acidified GaInSn media only. Our previous investigation suggests that sonication of acidified GaInSn media would lead to the generation of new active layers

and also prevent the system from attaining chemical equilibrium[3]. In this work, by ultrasonication of the methyl orange and GaInSn, we continuously created new GaInSn interfaces which reacted with the methyl orange and breaks the organic molecule apart, creating a new fluorescent material which was analysed to be composed of graphene quantum dots (GQDs). The GQD was characterized using transmission electron microscope (TEM), energy-dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), and Raman spectroscopy while the clear supernatant was analyzed using UV-Vis spectroscopy, and high-performance liquid chromatography. Further analysis of the GQDs indicated that the diffraction size is 0.28 nm and EDX analysis show its mainly composed of carbon. Moreover, sonocatalytic efficiency of 99.31% was achieved and maintained to about 97.87 % up to the fourth run. Identical results were obtained when the technique was extended and applied to other azo dyes (Eriochrome black T and Congo Red). These results for the sonocatalytic degradation of organic dyes specifically azo dyes using either liquid metal galinstan or gallium at elevated temperature shows its potential application in commercial environmental remediation processes and utilization for intermediate chemical production.

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D8. Electrochemistry and X-ray Photoelectron Spectroscopy of Immobilized Proteins on Self-Assembled Monolayers on Gold Electrodes

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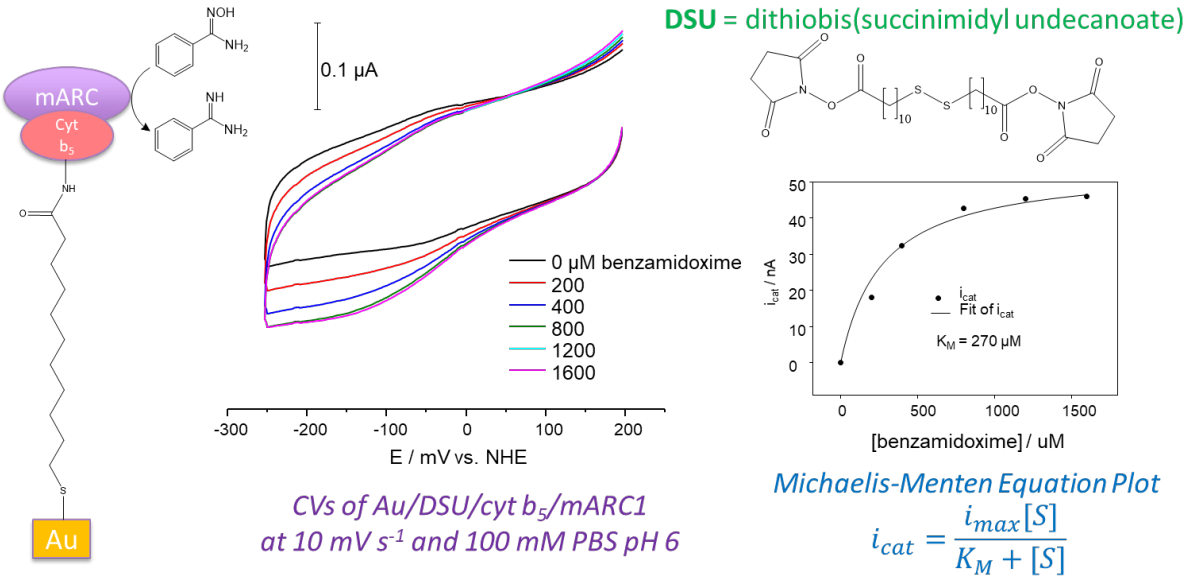
Electrochemistry of metalloenzymes is useful in understanding their redox properties for various applications such as biosensing and fuel cell development. Immobilization of enzymes on electrodes is crucial for developing stable and practical devices. Organothiols are widely used in forming self-assembled monolayers (SAMs) on gold electrodes because they readily form strong Au-S bonds. Terminal functional groups on SAMs control the type and strength of protein-monolayer interactions. In this work, Au electrodes were modified with mercaptocarboxylic acids reacted in situ with *N*-hydroxysuccinimide, a known protein cross-linking agent. Cytochrome c and human sulphite oxidase were immobilized on modified Au electrodes, as evidenced by the $Fe^{III/II}$ redox couple from the heme cofactors on the cyclic voltammograms (CVs). Monolayer and protein surface coverage on Au electrodes were determined from CVs. High resolution X-ray photoelectron spectra of cytochrome c on Au SAMs were consistent with immobilization of the protein. Au electrodes were also modified with dithiobis(succinimidyl) propionate (DSP) and dithiobis(succinimidyl) undecanoate (DSU). Human amidoxime reducing component (mARC) is a molybdoenzyme that is known to reduce *N*-hydroxylated compounds such as amidoximes. Along with its natural electron transfer partner cytochrome b_5, mARC was immobilized on DSP- and DSU-modified Au electrodes with and without the promoter chitosan, respectively. CVs of the modified electrodes showed catalytic reduction of benzamidoxime, a known mARC substrate. The Au/DSP/cyt.b_5-chitosan/mARC electrode was stable and remained catalytically active towards benzamidoxime after >30 days. Electrochemical studies show a promising method in the screening of potential pharmaceutical mARC substrates and inhibitors.



CVs of Au/DSU/cyt b_5/mARC1 at 10 mV s^{-1} and 100 mM PBS pH 6

Michaelis-Menten Equation Plot

$$i_{cat} = \frac{i_{max}[S]}{K_M + [S]}$$

D9. Effects of Lability and Melting Point on the Formation of Metal Oxide Phases Obtained by Calcination of Mixed-Metal Metal-Organic Frameworks

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Calcination of metal-organic frameworks (MOFs) to produce templated nanoparticle@porous carbon materials is an emerging field of research that capitalises on both the stability of porous carbons and the versatility of MOFs. While the macrostructure of MOF crystals is largely maintained upon calcination, less is understood about the retention of order on the micro- and meso- scale in the derived material. Recent work in our group has demonstrated that zirconia nanoparticles formed via calcination of UiO-66 experience minimal migration, suggesting a degree of local order may be maintained in the derived material.[1]

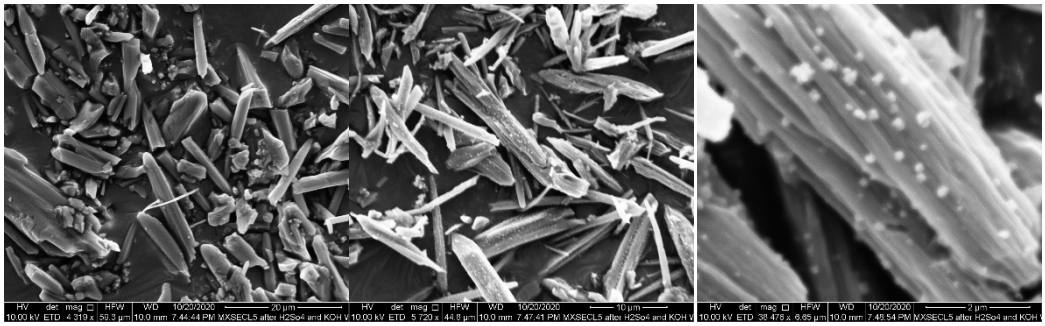

Figure 1: Pristine PCN-222-Cu (left) and PCN-222-Cu calcined at 800°C (middle and right)

In this work, PCN-222-M (M = Cu, Zn), a porphyrinic zirconium MOF with a secondary, non-structural metal incorporated into the porphyrin unit,[2] was calcined at a variety of temperatures to obtain nanoparticle@porous carbon materials. It was found that calcination of PCN-222-Cu caused the formation and sintering of copper oxide as nanoparticles on the surface of the material, while calcination of PCN-222-Zn did not result in the formation of analogous zinc oxide particles at the corresponding normalised temperature. This is hypothesized to be a consequence of the relative stability of the Cu–N and Zn–N bonds. Furthermore, higher calcination temperatures resulted in a greater degree of sintering of the copper oxide, thus suggesting a high level of control over copper oxide particle size is achievable.

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D10. First-principles study of the atomic volume of hydrogen in palladium

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The partial atomic volume of hydrogen, vH, is a fundamentally important thermodynamic parameter of interstitial metal hydrides in which dissociated H occupies interstices in the metal lattice. Such an important property should be able to be reliably calculated by a suitable theory or model in order to explain and understand its origin. In practice, vH is typically obtained by means of ab initio calculations founded on density functional theory (DFT), where the equilibrium lattice constant at zero temperature is found by minimising the Born-Oppenheimer energy. While the absolute lattice parameters calculated in this way depend quite strongly on the DFT scheme employed, the present work showed that vH is rather robust against differing calculational approaches, thus making a meaningful comparison of theory and experiment possible. A comparison between vH calculated for PdnH ($0 < n < 8$), employing DFT within the harmonic approximation, with in-situ neutron diffraction measurements revealed a significant discrepancy when octahedral-only interstitial occupancy was assumed. Calculations for PdH with mixed octahedral and tetrahedral occupancy suggested that PdH contains around 20% octahedral H.

E1. Design of surface-functionalised polycaprolactone: considering degradation and fate of modified biomaterials

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Polyesters including poly(ε-caprolactone) (PCL) are commonly used as biomaterials in tissue engineering. PCL is biodegradable, however it is hydrophobic and lacks functionality required for interaction with biological material (e.g. proteins). PCL can be surface-modified to introduce desired functionality and allow for protein binding.

Many recent studies on surface-modified polyesters have not investigated the effect of surface modification on the degradation of the substrate, or the fate of the surface layer itself.[1] Particularly when attaching a hydrophilic surface layer to a hydrophobic substrate it is important to assess if this modification will alter the degradation rate of the material's surface.[2]

In the present study PCL has been modified by gamma irradiation-induced grafting using two different monomers to introduce two different types of functionality. 2-Aminoethyl methacrylate (AEMA) has been used to introduce amines for conjugation to biopolymers that have good binding affinity for bone growth proteins, and 3-sulfopropyl acrylate (SPA) is used to introduce sulfonates for direct protein binding.

Optimisation of the grafting process is required as the graft copolymers are not biodegradable. Parameters including monomer concentration and radiation dose were varied in order to yield graft copolymers that are small enough to be cleared from the body. The surface layer stability was evaluated for modified PCL samples and it was found that the two relatively similar surface modification approaches resulted in vastly different stabilities of the graft copolymer in buffer solution.[2]

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E2. Dewetting of poly(lactic-co-glycolic): Problems when modelling nanoparticles with thin films

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Poly (lactic-co-glycolic acid) (PLGA) is a polymer commonly used in nanoparticle delivery systems due to its biodegradability through hydrolysis of the polyester functionality and post-modification potential. Characterisation methods to analyse the chemical and morphological features of the nanoparticle surface is limited in scope compared to thin film surfaces. As a result, it is simpler and often more convenient to model the surface modification of nanoparticles with thin film studies. Significant work has used polyester thin films to investigate surface modification and adsorption of *in vitro* proteins for application in analogous drug delivery systems[1-4].

Typical protocols for fabrication of thin films involves spin coating or dip coating of polymeric solutions onto pre-functionalised surfaces such as salinized silicon wafers or glass slides. When studied or modified in aqueous systems, amorphous polyesters of low Tg (<50 °C) are known to swell and hydrolyse, resulting in localised hydrophilic domains causing deformation to ease thermodynamic, mechanical and osmotic stress. Consequently, the hydrophilic polymeric material can retract from the hydrophobic surface it was forced to cover; a process known as dewetting. Dewetting is unique to thin film studies on hydrophobic surfaces causing thin films to behave in a manner inconsistent with nanoparticle surfaces.

This work utilises current advanced characterisation techniques to highlight the disjoint in using thin films to model nanoparticle surfaces, primarily caused by the dewetting process. Characterisation of PLGA thin films with ellipsometry, atomic force microscopy and X-ray photoelectron spectroscopy are judicially compared with nanoparticles analysed by dynamic light scattering.

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E3. Chemiluminescent Read-Out of Degradable Fluorescent Polymer Particle

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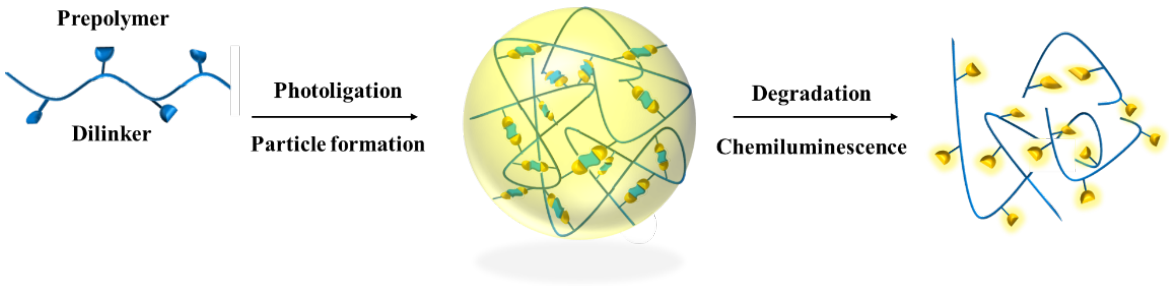
Polymer particles are an important and ubiquitous class of materials possessing an array of characteristics attracting wide-ranging application and continuous development. In line with the notion that integrative science can open up exciting and novel opportunities, modern photochemistry – with a focus on clean, efficient reactions, and longer wavelengths – presents a powerful interfacial and largely unexplored tool for particle design. Underpinned by unreported photochemical reactions, we have recently developed a new platform technology for particle synthesis.

Specifically, we reported how well-defined polymers functionalised with photo-active moieties (tetrazole[1] or ortho-methylbenzaldehyde[2,3]) can be rapidly cross-linked into functional microspheres under UV or visible irradiation. Similar to a precipitation polymerization technique, the synthesis does not require any stabilizers, bases or initiators, and proceeds at ambient temperature to yield to narrow disperse microspheres in less than 2 hours. Moreover, control over the concentration, solvent combination and irradiation intensity led to a broad and tunable particle size range (0.2 – 5 µm). Importantly, the novel properties of the resulting moieties were translated to the particles (e.g. inherently or on-demand fluorescent particles) and these can be further functionalized through residual acrylate, alkyne and hydroxyl groups. As a prime example, fluorescent particles were formed by crosslinking a photoreactive polymer and a peroxyoxalate dilinker. The self-reporting microspheres can be degraded on-demand by addition of hydrogen peroxide that cleaves the linking points and subsequently disintegrates the particles. Degradation of the microspheres can be readily monitored by the light emitted via chemiluminescence.[4]



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E4. Wavelength-Gated Softening of Hydrogel Networks

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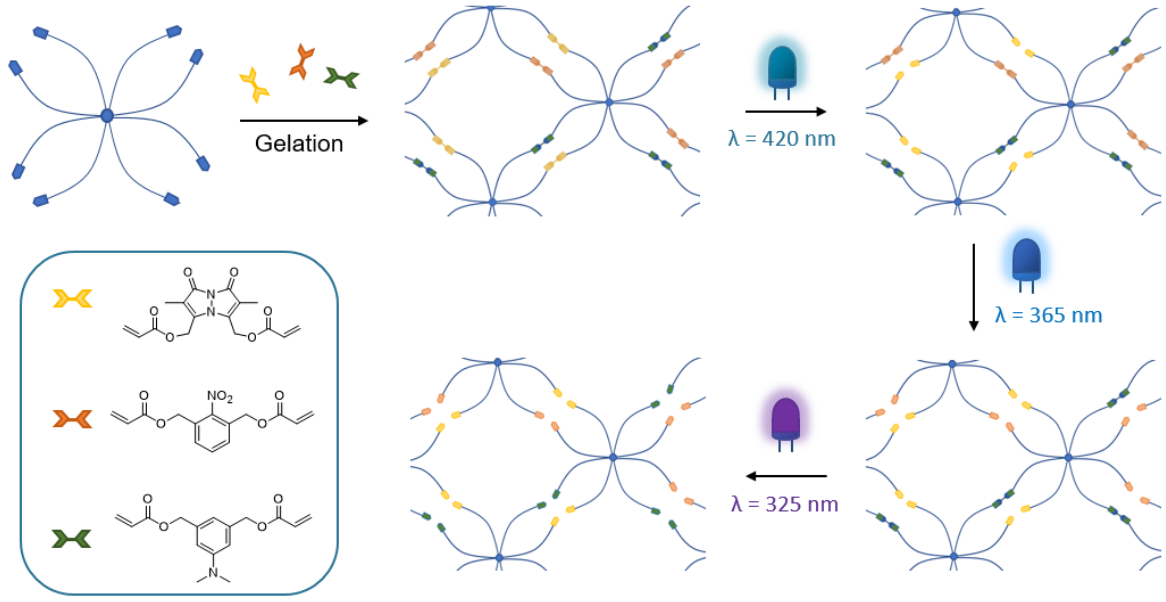
Hydrogels are water-swollen polymer networks that are widely used in biomedical applications including bio-sensing and drug delivery. Hydrogels with inherent light-responsiveness have the added benefit of being able to tune their properties in a spatial and temporal manner. Light-responsive hydrogels can be prepared via the incorporation of photoreactive groups within the polymer matrices. Thus, the chromophore determines the responsive character of the material and its absorption can be modified chemically to shift activation wavelengths or to change reaction kinetics entirely. Herein, three novel chromophores are synthesized and their photochemical activation wavelengths are thoroughly investigated before being incorporated into poly(ethylene glycol)-based hydrogels. The photodegradable linkers are based on acrylate derivatives of *ortho*-nitrobenzene (oNB), dimethyl aminobenzene (DMAB) and bimane moieties. The crosslinking process was induced at ambient temperature via a Michael thiol-ene addition of the crosslinkers to an 8-arm star PEG-thiol. Hydrogels with high mechanical strength could be readily formed within only a few minutes of mixing the precursors solutions.



Scheme 1: Crosslinking of an 8-arm star polymer and several chromophore linkers (yellow: bimane, orange: DMAB and green: oNB), forming a hydrogel. After irradiation with a specific wavelength, the chromophores can be cleaved selectively, yielding a stepwise degradation.

By combining several chromophores into one hydrogel, a stepwise degradation can be achieved selectively via different wavelengths of UV and visible light (Scheme 1). Such a stepwise degradation holds great potential for controlled release of distinct biomolecules depending on their size.

E5. Biodegradable Polymer Encapsulated Drug Nanoparticles for the Management of Lower Respiratory Tract Infections

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Lower respiratory tract infections (LRTIs) are one of the leading causes of deaths all over the world while currently available treatment draws attention to the innovation of novel treatment. Pulmonary delivery of drugs has been recognised as one of the most efficient routes of drug delivery to the targeted area. This study aims to develop nanoparticles of biodegradable polymer poly(2-ethyl-2-oxazoline) coated ciprofloxacin for pulmonary delivery from dry powder inhaler (DPI) formulations for the treatment of LRTI. Ciprofloxacin encapsulated poly(2-ethyl-2-oxazoline) nanoparticles were prepared in a straightforward coassembly reaction. Characterization of the prepared nanoparticles was done by Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS), Fourier-transform infrared (FTIR) spectroscopy, Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA). Drug loading and entrapment efficiency were determined by UV-Vis spectrophotometer analysis. DLS and Zetasizer determined the nanoparticle size ranging from 199.8nm to 352.9nm. Surface negative charge as measured by zeta potential tends to decrease with increase concentrations of ciprofloxacin. The SEM observation showed that all the nanoparticles were spherical with smooth surface. According to DSC, TGA and ATR-FTIR spectroscopy, ciprofloxacin crystallinity is lost when encapsulated in the nanoparticles, indicating it is uniformly dispersed as a solid state. Drug loading and entrapment efficacy were in between 20.94-67.59% and 21.40-74.16%, respectively. The findings showed that the prepared nanoparticles were suitable for DPI formulations. It is expected to have a promising prospect for pulmonary drug delivery of ciprofloxacin loaded polymer nanoparticles for the management of LRTI with a controlled release profile.

E6. Photo-Cross-Linkable Polymers for Inkjet Printed OLEDs

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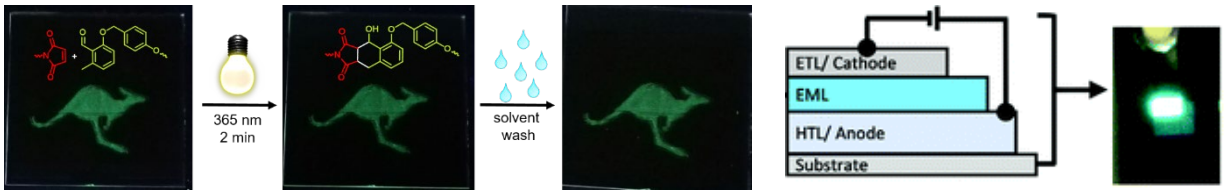
The rapid rise of Organic Light Emitting Diode (OLED) technology used in mobile device displays demands for the development of more efficient and economical manufacturing. While solution-based processes, such as inkjet-printing, are the most promising techniques to deliver this, the current obstacle that has yet to be overcome is the resolubilisation of previously deposited layers within multilayered OLED devices.

We introduce a catalyst-free, highly efficient, ambient temperature Diels–Alder reaction employing *o*-methylbenzaldehyde derivatives as photocaged dienes as an ideal approach for forming three-dimensional insoluble networks for inkjet printing of the OLED emissive layer. Herein, poly(methyl methacrylate) based polymers containing 4-(9H-carbazol-9-yl)-2-(3'-hydroxy-[1,1'-biphenyl]-3-yl)isoindoline-1,3-dione as a blue-green Thermally Activated Delayed Fluorescence (TADF) emitter and a photochemically active maleimide/*o*-methylbenzaldehyde cross-linker couple were synthesized and



their photo-cross-linking behaviour was studied.

While the network formation of the fluorescent films is evidenced by solvent resistance tests and monitored by FT-IR spectroscopy as well as ToF-SIMS, the surface roughness is investigated via Atomic Force Microscopy (AFM) and found to be unchanged by a solvent wash after the cross-linking. Time resolved fluorescence measurements confirm that the TADF properties are maintained upon integration in a polymer and HOMO/LUMO levels of the emitter species remain unchanged by the photo-cross-linking of the polymer chains. Furthermore, we demonstrate that the polymer solution can be printed on an inkjet-printer and subsequently photo-cross-linked for multilayer OLED device fabrication.[1] The resulting OLEDs have a peak emission wavelength of 520 nm with a maximum luminance of around 4700 cd m^2. The peak emission wavelength can be blue-shifted by exciplex management to achieve a peak wavelength of 494 nm.[2]

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E7. Visible Light Induced Reversible Ligations for Precise Soft Materials Design

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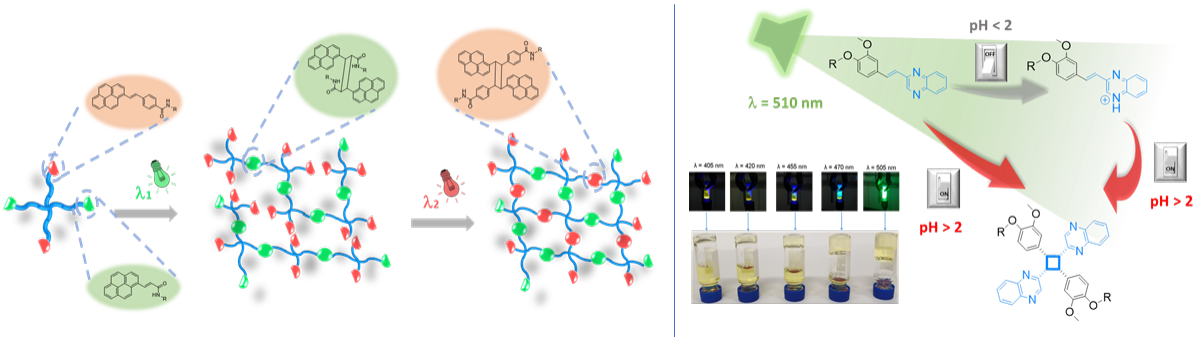
Photochemical reactions are important tools for soft matter materials design thanks to the spatiotemporal control they provide. [2+2] Cycloadditions are among the most powerful photoreactions as they can occur under catalyst-free conditions in a reversible fashion. However, the majority of [2+2] cycloadditions require UV light initiation, which is harmful to living cells and drastically limits their applications in the biological and biomaterials realms.

Since the activation wavelength of [2+2] photocycloadditions highly depends on the electronic structure of the molecules, we have achieved red-shifting of activation wavelengths (up to 550 nm) by synthetically extending the conjugated system or adding electron donating or withdrawing groups.[1-2] To monitor the wavelength dependent reactivity of this type of reactions with the constant photon counts, it is critical to experimentally record the so-called action plots, as it was already shown by our group that the wavelength where the reactivity is maximum, is usually not aligned with the absorption maximum of the chromophores. [1-2]



Other additional features such as solvent or pH-dependent reactivity and ⍰-orthogonality of the chromophores enable precise control over the soft materials design. So far, we have demonstrated that the physical properties of crosslinked network of polymers, also known as hydrogels, can be tuned by using two different chromophores, which have distinct reactivities at different wavelengths[1] as well as being able to control the photo-crosslinking of hydrogels by tuning the pH of the reaction environment.[2]

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E8. Photocycloadditions in Disparate Chemical Environments

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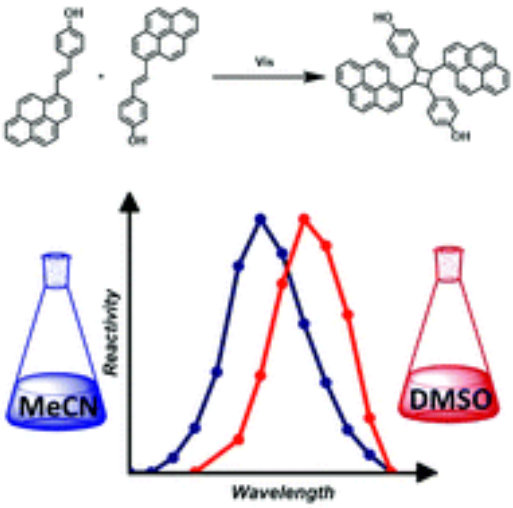
Photochemistry offers various advantages over conventional chemistry such as spatiotemporal control and the ability to selectively trigger reaction channels using different colours of light. Even greater control over complex ligation systems can be achieved if multiple molecules can be addressed independently, with one wavelength activating one molecule while another molecule remains untouched until it is activated by a disparate wavelength. While such *I*-orthogonal reactions in principle can be carried out using LEDs, precise mapping of the wavelength-dependent reactivity of all involved reactions partners is required since it cannot be readily predicted from absorption spectra. This can be achieved by measuring so-called action plots, where a photoreactive molecule is irradiated with specific wavelengths using a nanosecond pulsed laser system and the reaction conversion is plotted *versus* the irradiation wavelength.

The [2+2] cycloaddition of styrylpyrene is particularly suited for *I*-orthogonal ligation reactions, since it can be triggered at higher wavelengths, whereas light of shorter wavelengths favours the cycloreversion and can therefore be employed to actively supress the [2+2] cycloaddition, while simultaneously triggering a second photoreactive molecule. Styrylpyrene has been employed for several photoligation reactions over the last few years, yet critical reaction parameters remain unexplored.

We herein elucidate the wavelength dependence of the photocycloaddition of styrylpyrene by (i) accessing action plots dependent on the reactivity relative to the number of absorbed photons, (ii) establishing the effect on substrate concentration on photochemical reactivity and (iii) determining wavelength-dependent reactivity as a function of the solvent environment, comparing acetonitrile with dimethyl sulfoxide.



Marschner, D. E., Kamm, P. W., Frisch, H., Unterreiner, A.-N., Barner-Kowollik, C., *Chem. Commun.,* **2020**. DOI: 10.1039/D0CC03911J

F1. Exploring energy transfer in NIR emitting bimetallic *d-f* bisterpyridine complexes

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In addition to organic ligands, photoactive transition metal complex derivatives have been exploited as light harvesting antenna to sensitise Near Infra-Red (NIR) emission from Yb(III) and Nd(III) containing complexes. We have recently shown that $Ru(tpy)_2^{2+}$ derivatives can be effective in sensitising NIR luminescence from the Nd(III) and Yb(III) cations via energy transfer from the metalloligand ^{3}MLCT state to the Ln(III) excited state.

There are several physical and electronic properties of an antenna which significantly influence the rate and efficiency of Electronic Energy Transfer (EET). These properties include the metal to metal distance, the connectivity between the metal centres, the excited state lifetimes as well as the nature of the excited state. For bimetallic systems bridged by a rigid organic ligand, the properties of the antenna complex can be controlled via modification to the ditopic bridging ligand.

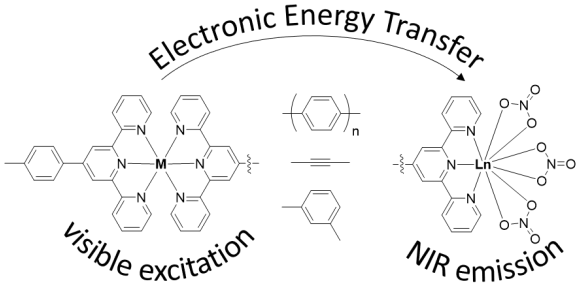

Figure 1. Antenna process of sensitized NIR emission where M = Ru(II), Ir(III) , Os(II) and Ln = Nd(III), Er(III) and Yb(III)

Herein, we have synthesised and characterised a series of bisterpyridine metalloligands (Fig.1), altering the connectivity between the terpyridine metal binding sites, coordination environment and transitions metal species, allowing the coordination and photophysical interactions with several Ln(III) cations (Ln = Yb, Nd, Er and Lu) to be explored. Using a combination of steady state, time resolved and ultrafast transient absorption experiments, the efficiency and mechanism of the energy transfer leading to the observed NIR luminescence has been characterized.

F2. Construction of enantiopure photoactive Ir(III)-containing tetrahedra

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The design and assembly of discrete multi-component metal–organic cages, with specific configurations and well-defined cavities, from directional bridging ligands and geometrically pre-oriented metals is emerging as an appealing topic in recent supramolecular coordination chemistry.[1,2] In addition, the controlled self-assembly of enantiopure cages is of particular importance because of their potential applications as enzyme mimics for stereoselective recognition and catalysis.[3]

Given its predictable geometric orientation, kinetic stability and robust photoluminescent properties, the *fac*-Ir(ppy)$_3$ motif (ppy = 2-phenylpyridinato) is an ideal building block for the incorporation into chiral photoactive supramolecular structures. Taking advantage of the kinetic inertness of Ir(ppy)$_3$ unit,, we propose a step-wise metalloligand approach whereby chelating moieties, which are attached to the inert core, can coordinate labile metals and facilitate the self-assembly process.

Previously, we synthesised an achiral Ir(III)-containing metalloligand consisting of three 2,2':6',2''-terpyridine units appended to a *fac*-Ir(ppy)$_3$ core via phenylene linkers. Reaction with Zn(II) leads to the formation of $[Ir_4Zn_6]^{12+}$ tetrahedra where all *T*, *S*$_4$ and *C*$_3$ diastereomers are observed. To eliminate the formation of mixed stereoisomers, we have developed a method to resolve the metalloligands into the enantiopure Δ/Λ isomers which involves modification of the Ir(ppy)$_3$ core to integrate a chiral pinene motif, allowing for the construction of enantiopure photoactive metallo-supramolecular tetrahedra.

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F3. A comparison of intra- vs intermolecular energy transfer between 4f metal ions using heteronuclear bimetallic supramolecular helicates

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The incorporation of Lanthanide ions (Ln^{III}) into supramolecular assemblies has been an increasingly prevalent topic in recent literature with a steady flow of helical, tetrahedral and cuboid structures appearing. Many of these combine the unique structural properties and characteristic emission of Ln^{III} cations to develop new materials for probes or sensors.[1] Energy transfer between Eu^{III} and Nd^{III} has been previously investigated, detailing dual visible and NIR emission, with notable quenching of Eu^{III} emission in the presence of Nd^{III}.[2]

We report a series of homometallic and heterometallic Ln_2L_3 helicates (Ln = Eu^{III}, Nd^{III}) prepared via self-assembly using a dipicolinate based bis-tridentate chelate (L). Five molar ratios of Eu^{III} : Nd^{III} (100:0 70:30, 50:50, 30:70, 0:100) were used to produce statistical mixtures of Eu_2L_3, $EuNdL_3$ and Nd_2L_3. These helicates were characterised through high resolution mass spectrometry and NMR techniques.

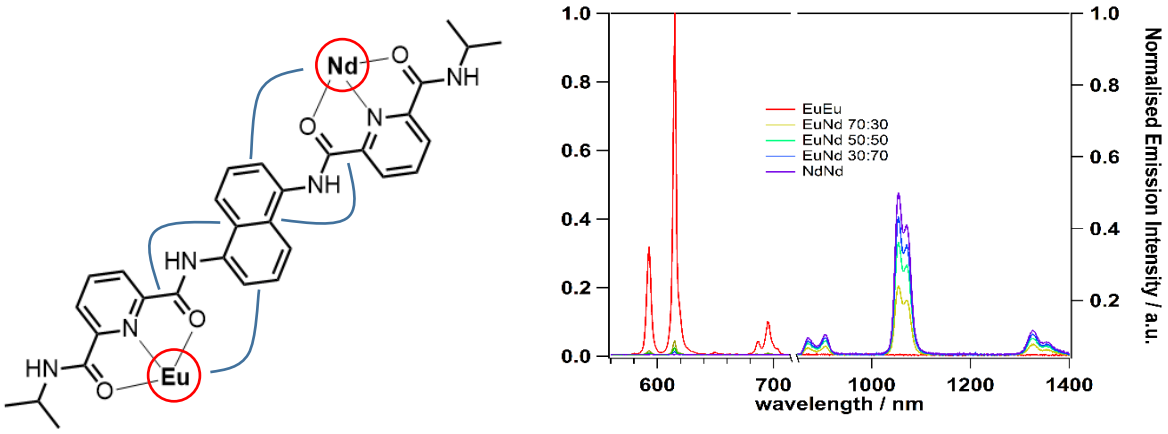

Figure 1. Schematic representation of an $EuNdL_3$ heterometallic helicate (left). Emission of the series of complexes showing significant quenching of Eu^{III} emission when in the presence of Nd^{III} (right).

In the presence of Nd^{III}, the characteristic Eu^{III} emission is significantly quenched, while Nd^{III} emission remains proportional to the amount of Nd^{III} present. Moreover, luminescence lifetime measurements resulted in the elucidation of biexponential decay behaviour when monitoring Eu^{III} emission at 615 nm. We propose the observed quenching of the longer lifetime can be attributed to intermolecular energy transfer from Eu_2L_3 in solution to both $EuNdL_3$ and Nd_2L_3, while the second, much shorter, lifetime represents intramolecular energy transfer within the $EuNdL_3$ helicates. In all cases, since the excited states of Nd^{III} are at lower energy than those of Eu^{III}, the former acts effectively as an energy sink, leading to a significant decrease in the intensity of the Eu^{III} emission.

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F4. The Balancing Act of Stabilising High Oxidation States of Copper and Nickel with Redox Non-Innocent Ligands containing Thiosemicarbazone and Dithiocarbazate Schiff Bases

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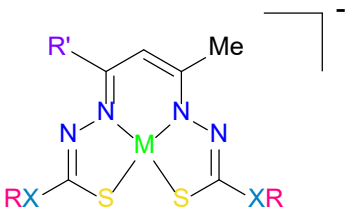
The use of N,S chelating ligands such as thiosemicarbazides and dithiocarbazates provide an excellent environment to complex transition metals in a variety of oxidation states. Complexes of Cu(III) and Ni(III) are rare (compared to Cu(II) and Ni(II)) and are not often isolated as stable entities, but have been proposed as transient intermediates in some reactions. The general requirements for stabilising high oxidation states stem from the nature of the donor atoms, the degree of electron delocalisation, the size of the chelate rings, the use of electron donating groups and the formal charge on the ligand to balance the high charge of the metal ion.

Combining the β-diketone acetylacetone with 2 equivalents of the relevant thiosemicarbazide or dithiocarbazate produces a tetradentate N_2S_2 ligand that is suitable for stabilising high oxidation states according to the above specifications. These two families, acetylacetone bis(thiosemicarbazone) and acetylacetone bis(dithiocarbazate) Schiff bases, were investigated here in complex with Cu and Ni.



$[M^{II}(acacR)]^-$ M = Ni, Cu X = NH, R = Me, Et, Ph, Al, R' = Me
$[M^{II}(banR)]^-$ M = Ni, Cu X = NH, R = Me, Et, Ph, R' = Ph
$[M^{II}(acacsR)]^-$ M = Ni, Cu X = S, R = Me, Bn, R' = Me

F5. Mechanistic Exploration of Elastically Flexible Crystals by Automatic Analysis

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A recent surge in reports of crystals exhibiting elastic flexibility has generated excitement regarding their potential applications in flexible electronics. To fully realise these applications, comprehensive understanding is required to explain why some crystals can be tied into knots, while others are extremely brittle. Different rationales for elastic flexibility have been proposed: many crystals have been engineered to impart flexibility through isotropic interactions, while other flexible crystals have anisotropic interactions[1]. Clearly, there is no 'one mechanism fits all' when it comes to elastic flexibility in single crystals. The mechanism of flexibility in elastic crystals can be resolved on an atomic-scale by use of micro-focused synchrotron radiation[2]. By examining the crystal structure at multiple positions across a bent crystal, the deformations of the cell parameters can be quantified (Figure 1). A wide range of crystals have been analysed using this technique to determine their respective mechanisms; however, structural mapping quickly produces large volumes of data, and manual processing is inefficient when only subtle changes are observed. Instead, software was developed to automatically process these datasets by turning raw diffraction images into finalised CIF files with graphical analyses. This software is also applicable to the analysis of other large crystallographic datasets, such as variable temperature experiments, as it provides a foundation to quickly analyse large volumes of diffraction data.

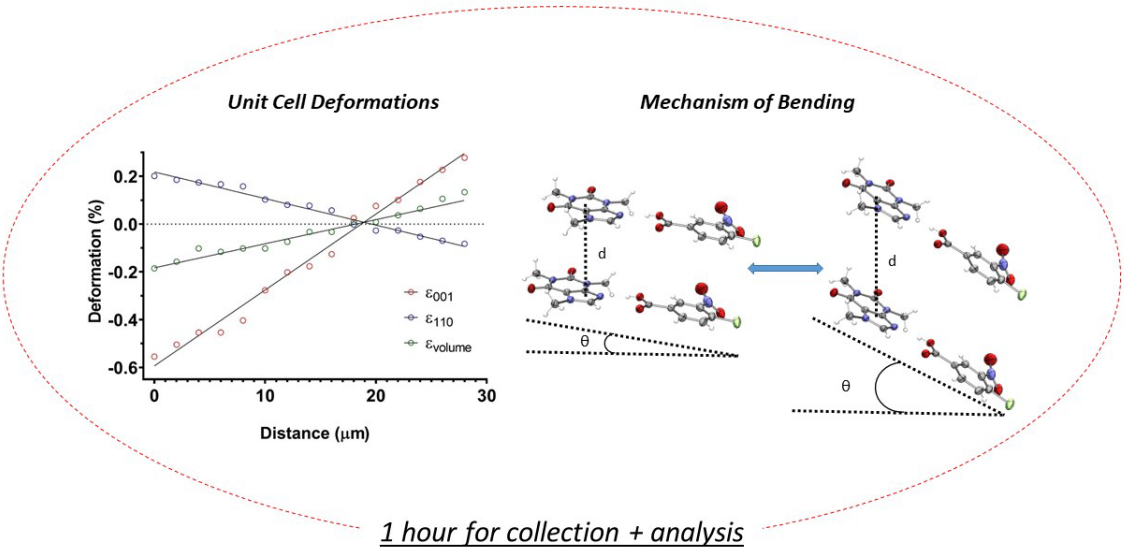

Figure 1: Unit cell deformations and the corresponding mechanism of elasticity for co-crystals of caffeine and 4-chloro-3-nitrobenzoic acid.

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F6. Using Cu(I) for Earth Abundant Photocatalytic Metallo-Supramolecular Cages

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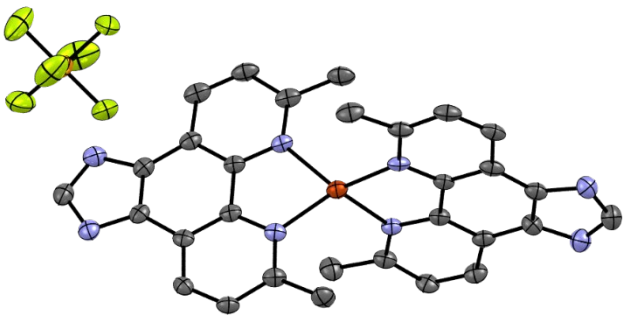
With the growing synthetic complexity of modern drugs and natural products research, considerable attention has been paid to less traditional synthetic approaches, such as visible light photoredox catalysis.[1] Most reports make use of precious metal-containing cyclometalated Ir(III) or polypyridyl Ru(II) complexes, due to their long-lived excited states, stability and strong absorption in the visible region.[1]

One disadvantage of this approach is the low abundance of iridium and ruthenium which increases their cost. An alternative to these catalysts are Cu(I) polypyridyl complexes, which have been shown to possess many of the desirable features of their precious metal counterparts, while being substantially cheaper.[2]

In addition to their use as discrete catalysts, there has been growing interest towards including photocatalytic units into supramolecular assemblies.[3] These assemblies can act as nanoscale reactors, which upon guest binding, can provide engendered control allowing what is synthesised within the cavity to differ considerably to what is synthesised without.[4]

The present study reports the functionalisation of 2,9-dimethyl-1,10-phenanthroline ligands with bridging imidazole moieties at the 5,6 position, to yield Cu(I) complexes which provide linear connectivity. Photophysical and electrochemical characterisation of these complexes indicate the desired properties of the complexes are retained post modification. Combining these ligands with preformed organic corners has allowed the first steps to be taken towards supramolecular Cu(I) cages with well-defined internal volumes, as well as desirable photophysical and electrochemical properties.



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F7. An Electrogenerated Organocopper(II) Reagent for the Formation of Carbon-carbon bonds

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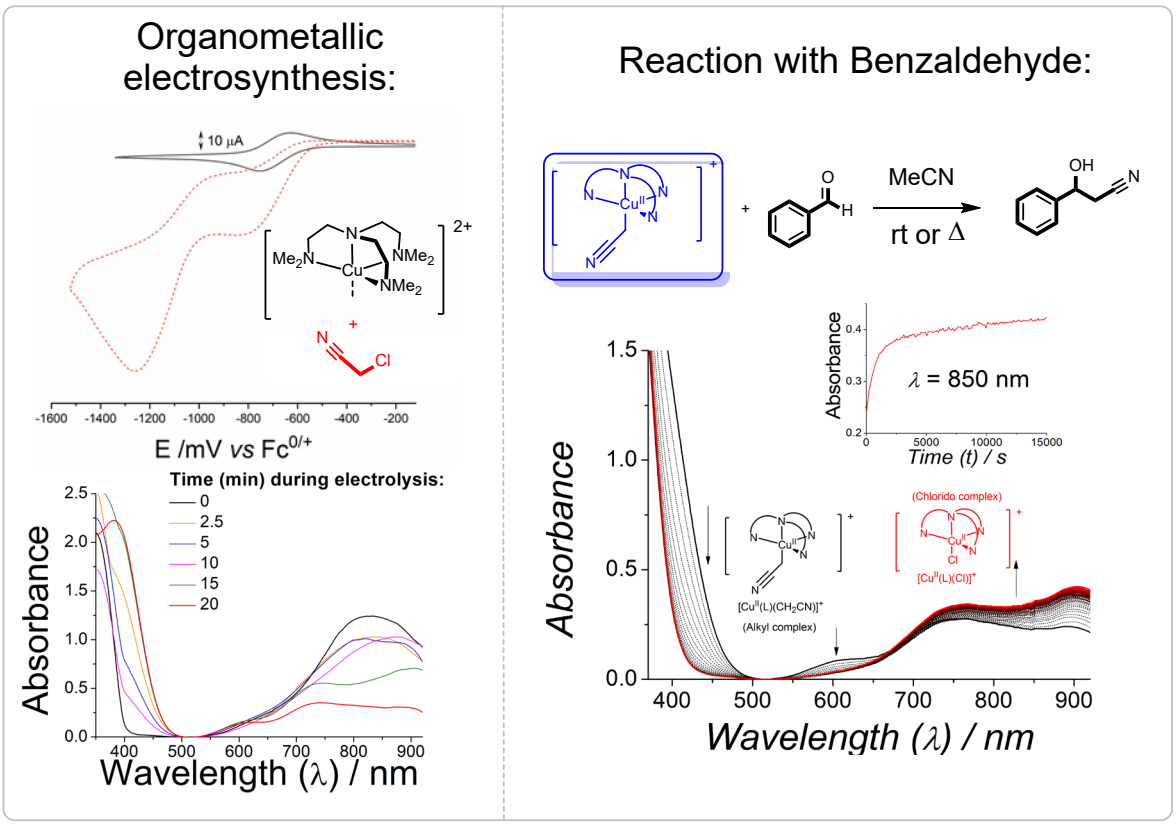
Once overlooked, electrosynthesis has recently become a topic of growing interest in the pursuit of organic molecules with high complexity. The environmentally benign nature of this technique, and the fact that it allows virtual control of a reaction by modulating the applied potential have proven that electrosynthesis can be an effective alternative to classical synthesis.[1]

This talk comprises a novel strategy towards the formation of carbon-carbon bonds promoted by an electrogenerated organocopper (II) species. Namely, two electrogenerated species -- a copper(I) complex bearing a chelating ligand $[Cu^{I}L]^{+}$, and a cyanomethyl radical ($\bullet CH_2CN$) react *in situ* to produce the organometallic $[[Cu^{II}(L)(CH_2CN)]^{+}$.[2] This species is then reacted with benzaldehyde, formally acting as a nucleophile to promote the addition of the cyanomethyl moiety into the carbonyl. Current experiments are focused on exploring the mechanisms of this reaction, which may provide additional knowledge within overlapping fields such as metal-mediated radical polymerisations.[3]



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G1. The Design, Application and Evaluation of a Gamified Virtual Laboratory to Aid in Distance Learning.

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With a growing demand for distance learning and open universities, combined with recent advances in technology, interest has turned to developing virtual alternatives to the traditional "hands-on" chemistry laboratories. With a larger proportion of tertiary students studying off-campus, these laboratory experiences need to be interactive, engaging, and informative to adequately substitute the laboratory experience. Here we describe the generation and investigation of a gamified, interactive virtual laboratory tool as both a replacement and as an additional resource to the traditional aspirin synthesis laboratory experiment.

Preliminary feedback from these two delivery formats indicates that off-campus students enjoyed, and were engaged with the interactive format, praising the one-on-one style experience and the ability to revisit areas of concern. Students utilising the virtual laboratory as a supplementary tool for their traditional laboratory experience also appreciate the opportunity to revisit areas of uncertainty, however, do not require the interactive tools as these skills had already been achieved in the physical laboratory. Overall, this investigation shows promise for the interactive virtual laboratory as a beneficial resource for both complimenting the laboratories and acting as a substitution for the traditional laboratories.

G2. Mobilising molecular models across the COVID campus

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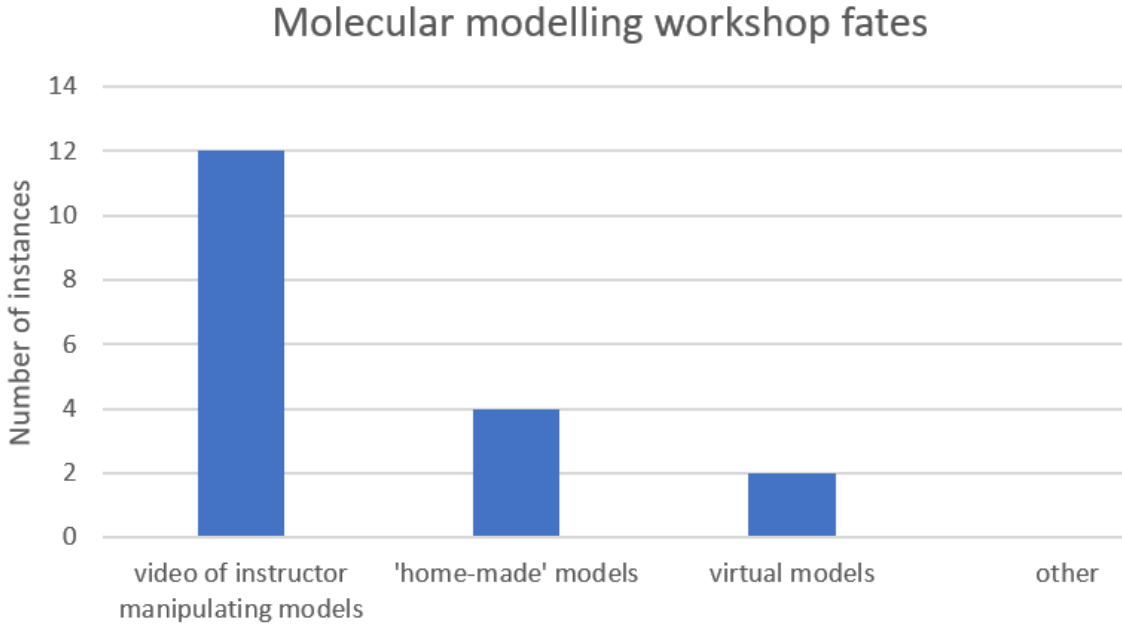
Chemistry as a discipline relies on cognitive interactions with models of atoms/molecules[1,2]. Although molecular dynamism highlights the limits of molecular modelling[3], there is still consensus that modelling chemical structures is epistemologically pragmatic[4] and realistic[5]. While modelling can be performed through drawing, the representation of 3D structures in 2D sketches requires extensive visuospatial interpretation[6]. Physical molecular modelling kits overcome these limitations. Given that first-year chemistry students struggle to simultaneously develop analytic strategies while grappling with 3D visualisation[7,8], molecular models offer a pedagogically pragmatic learning support tool for this cohort[9,10].

Despite its pedagogical niche in chemistry, molecular models are physical resources and therefore have a limited mobility. It is no surprise that COVID-19 has diffused university campuses worldwide into predominately digital networks[11]. The digital learning immaturity in the higher education sector[12] together with the rapid and under-funded digital transformation required of universities in early-mid 2020[13] leaves little consideration for physical learning resources. There is currently no peer-reviewed literature of molecular model use in education since the arrival of COVID-19. I have therefore analysed YouTube uploads from chemistry instructors to determine how they have adapted traditional molecular modelling workshops for online learning. From this analysis, three fates for molecular models emerge: they are constructed with at-home items, manipulated and filmed by the instructor, or replaced with a virtual modelling tool. None of these approaches fully exploit the pedagogical value of molecular modelling kits. I will discuss the need to better utilise our molecular modelling kits for our chemistry students in a COVID world.



Summary of molecular model videos made by higher education staff in response to COVID-19-driven online learning to replace hands-on model learning. YouTube search made on 22/10/2020 for “Molecular Model” – results were filtered for 2020 only.

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G3. Zoomed-in Science: Connecting Real Scientists with Primary School Classes Over Zoom

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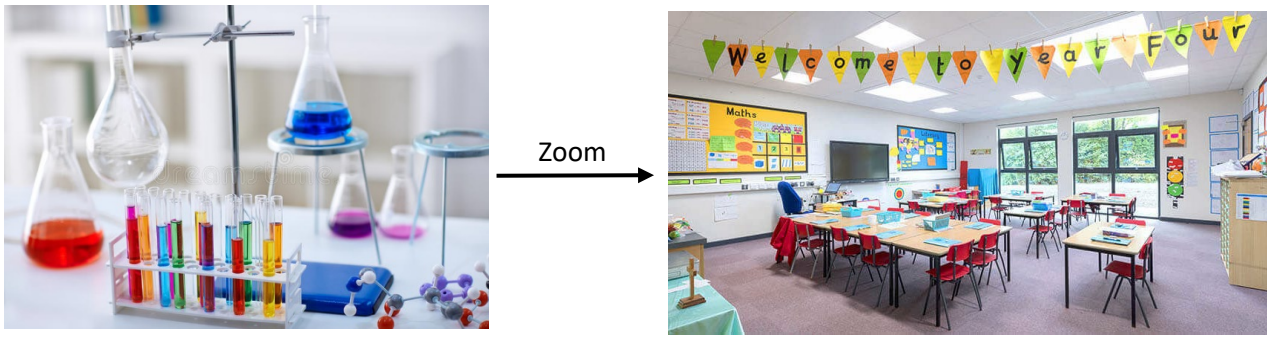
"Zoomed-in Science" is a newly developed outreach program that connects university scientists with primary school classes over Zoom-type streaming services. Presenters such as HDR students, ECRs or academics will carry out short (10-20 minute) scripted sessions directly from their research laboratory, which will be comprised of a mixture of visually appealing scientific demonstrations along with explanations of the science behind them, thought provoking follow-up questions as well as answering an questions the class might have. The content of the sessions is aligned with the Australian curriculum and is carefully tailored to enhance engagement to the class's current unit of study.

This program will offer scientists at all levels (undergraduate to PhD and beyond) a unique opportunity to provide service to their scientific community with minimal time or financial commitment, without even leaving the lab, all while having a lot of fun inspiring minds that will ultimately shape the future of STEM research in Australia. Zoomed-in Science will be supported by QUTs Centre for Materials Science and the Royal Australian Chemical Institute and aims to begin working with primary schools in q1 2021. The program endeavours to cover many areas of science and engineering starting with chemistry and physics.



Further details of the motivations, design, goals and opportunities surrounding the program will be discussed along with the perceived benefits for students, scientists, teachers and research. Please feel free to contact me directly if you are interested in finding out more or becoming involved!

G4. Understanding a stereoselective P450 epoxidation through a synthetic comparison

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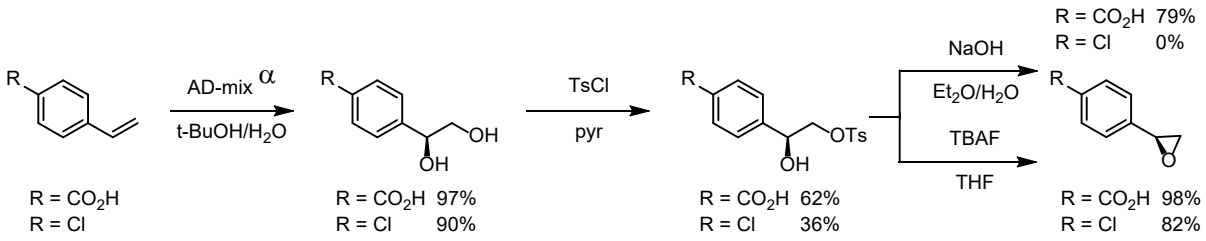
Wild-type CYP199A4 from *Rhodopseudomonas palustris* has previously been found to oxidise a variety of functional groups of para-substituted benzoic acids opposite to a carboxylate directing group. A particularly intriguing reaction within this set was the conversion of 4-vinylbenzoic acid into 4-(oxiran-2-yl)benzoic acid. In order to determine the enantiomeric preference of the enzyme, pure product standards of R- and S-epoxides were required.

The desired compounds were synthesised through a three-step synthesis from 4-vinyl benzoic acid, featuring an intramolecular nucleophilic substitution of an enantiomerically-pure species to give the desired chiral epoxides (Scheme 1). Stereochemical assignments throughout the synthesis were established through a combination of crystal structure data, comparison of optical rotation to literature values for an analogous 4-chloro species, and the mnemonic used to predict the stereochemical outcome of Sharpless asymmetric dihydroxylations.



Scheme 1: Synthesis of enantiomerically-pure benzoic acid and chlorobenzene epoxides.

Analysis of (R)- and (S)-4-(oxiran-2-yl)benzoic acid via enantioselective HPLC gave strong indication that CYP199A4 converts 4-vinylbenzoic acid almost exclusively into the (S)-epoxide via co-elution of this species with the enzymatic product. Significantly, conversion to the S-epoxide is in contrast to products of hydroxylation reactions with CYP199A4, where C-O bond formation occurs on the other face of the molecule.

G5. Chemical composition of traditional medicine plants: *D. obscura* root bark

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This work seeks to phytochemically characterise plants used in the traditional medicines of the Australia Aboriginal and Torre Strait Islander communities of the Northern Territory. This research is a collaborative endeavour between UQ, Integria Healthcare®, Menzies School of Health and Traditional Homeland Enterprises.

The phytochemical profile of the endemic Australian plant *Denhamia obscura* has not previously been reported, despite its traditional use dating back eons. Research into the chemical composition of the root bark from this plant was carried out, since this is the part traditionally used as an oral anaesthetic. We report the isolation and characterisation of seven known pentacyclic triterpenes and eight known diterpenes belonging to the abietane family of compounds (Figure).

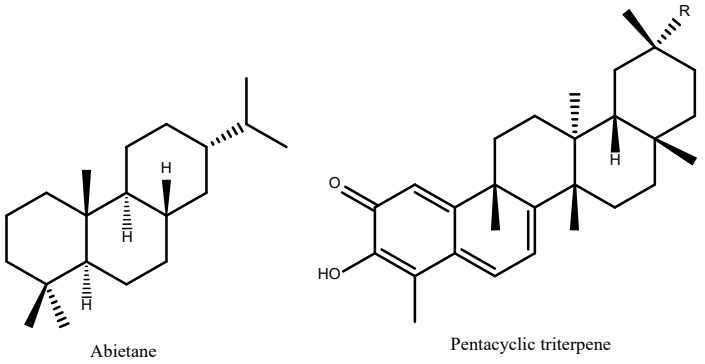

Figure: Abietane and an oxidised pentacyclic triterpene, simplified core structures for reference

In addition to chemical characterisation, the crude extract and the four most abundant compounds were tested for antibacterial, anti-inflammatory, and cytotoxic properties. Preliminary antimicrobial and anti-inflammatory assays of the crude extract informed the elucidation of the chemical composition of *D. obscura*, as well as potential alternative uses of this plant. The antimicrobial tests showed that the root bark extract displayed activity against *S. aureus* and *S. pyogenes.* Similarly promising anti-inflammatory activity (NF-kB test) was found. Results associated with the most abundant compounds will be discussed.

G6. Australian grown Feijoa (*Acca sellowiana*) – an underestimated fruit?

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The present study determined the (bio)chemical composition and biological properties of Australian grown feijoa (*Acca sellowiana*), in order to assess the nutritional quality and antimicrobial activity of this emerging subtropical/tropical fruit. Polyphenolic compounds and vitamins were determined by UHPLC-PDA-MS/MS, showing that the feijoa fruit not only contains high amounts of antioxidant flavonoids, but is also a valuable source of vitamin C (63 mg/100 g fresh weight (FW)) and dietary fibre (6.8 g/100 g FW). The edible fruit peel possesses higher ($p<0.05$) amounts of antioxidant flavonoids and vitamin C than the fruit pulp. This is most likely the reason for the observed strong antimicrobial activity of the peel-extracts against a wide-range of food-spoilage microorganisms. The consumption of feijoa fruit can deliver a considerable amount of bioactive compounds such as vitamin C, flavonoids and fibre, and therefore, may contribute to a healthy diet. However, short-term clinical trials and intervention studies are warranted to determine the actual bioavailability of the main nutrients and bioactive compounds as well as the potential health benefits of feijoa fruit consumption for humans. Furthermore, the potential use of feijoa-peel as a natural food perseverative needs to be investigated in follow-up studies.

Acknowledgement: This project was funded by the Australian Government and Produce Art Ltd. (Rocklea, QLD, Australia) via the Innovation Connections Grant Scheme and jointly supported by the Queensland Government, Department of Agriculture and Fisheries and the University of Queensland, Australia.

[Phan ADT, Chaliha M, Sultanbawa Y, Netzel ME (2019) Nutritional Characteristics and Antimicrobial Activity of Australian Grown Feijoa (*Acca sellowiana*). Foods 2019, 8, 376. http://doi:10.3390/foods8090376]

G7. Stingless bee honey as a unique source of trehalulose

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Stingless bees (tribe: Meliponini) are a diverse group of more than 500 known species that occur in tropical/sub-tropical regions, and are lesser known for their honey products than honeybees (*Apis mellifera*). Honey from stingless bees has long been prized by Indigenous communities worldwide for its health benefits.[1] In contrast to honeybees, a stingless beehive produces less than one kilogram per year, making it a rare resource, and valuable to the bees as food for themselves and their larvae. In warmer climates, the hive can produce excess honey,[2] and when harvested, stingless bee honey is valued for its depth of flavour. We tested stingless bee honey from 5 species, two from Australia, two from Malaysia and one from Brazil and found high levels of an unusual disaccharide, which was isolated, examined by LC-MS/MS and NMR and identified as the sucrose isomer, trehalulose. Analysis by high performance ion chromatography with pulsed amperometric detection of 36 honey samples from Australian and Malaysian species showed that the amount of trehalulose ranged from 17 – 58 g/100 g honey, present together with fructose and glucose. New work aims to understand the origin of this disaccharide in stingless bee honey and to provide an understanding of how to optimise the levels present in the honey. Trehalulose has not been identified as a major component in any other food. As such, the presence of trehalulose will increase the value of stingless bee honey due to the disaccharide's known bioactive properties.

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G8. Explorations into a new synthetic route to L-hexoses

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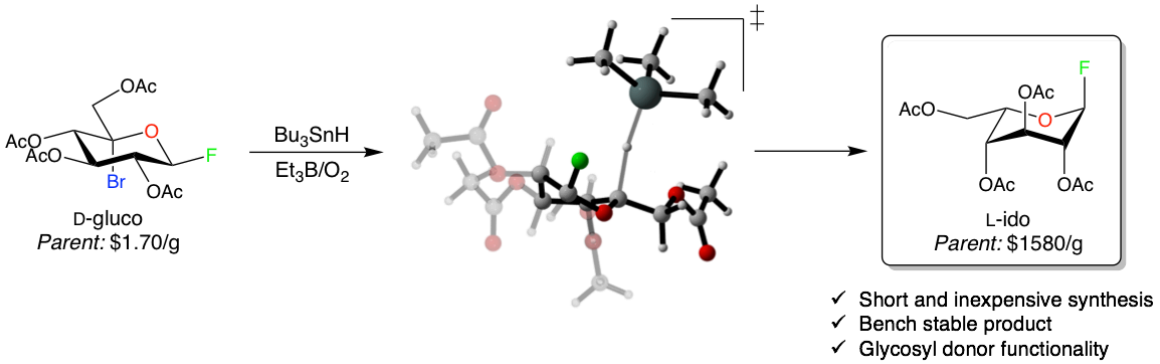
Rare and prohibitively expensive L-hexoses are accessible via C-5 epimerisation of suitably functionalised D-hexoses. We have previously confirmed that the reduction with tributyltin hydride of an acetate-protected D-glucuronide proceeds with complete selectivity for the L-ido product when the anomeric substituent is a β-F.[1] In our current study, we investigated the breadth of the scope of this reaction. Specifically, the influence of the protecting group choice, the identity of the C-6 substituent and the absolute configurations at C-2 and C-4 on reduction selectivity were all examined. We report the synthesis of a range of novel 5-*C*-bromo-β-D-glycosyl fluorides and the selectivities that are measured upon free radical reduction. We demonstrate that a combination of a β-F and a methoxycarbonyl group at C-5 is key to optimising selectivity for the L-ido product. DFT calculations explain why this combination of substituents is critical to the selectivity. This result provides a key step forward in addressing the general lack of understanding about how to synthesise L-hexoses selectively.



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G9. Dual-Wavelength Gated *oxo*-Diels-Alder Photoligation

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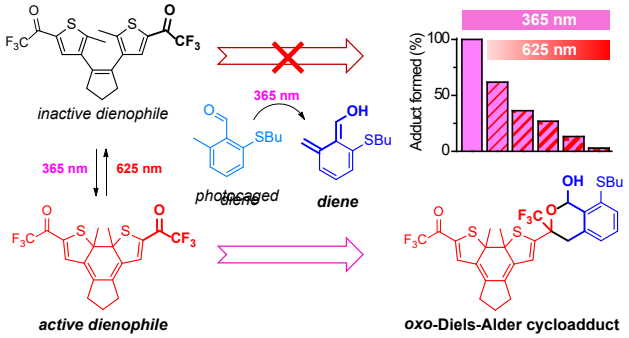
Photoinduced ligation reactions are essential tools for the chemical functionalization of molecules and materials in a variety of areas, such as polymer network formation, surface patterning, 3D printing, and bioconjugation. Most of these reactions can be regulated with one color of light, whereas two colors of light would be highly beneficial and improve the spatial resolution. Only a limited number of two-color controlled photoreactions have been reported to date.

We herein introduce a photochemical reaction system whose reactivity is controlled by two colors of light. Specifically, λ_1 (365 nm) induces the formation of a photocaged diene based on *ortho*-quinodimethanes able to undergo rapid cycloaddition with activated dienophiles, while λ_2 (625 nm) regulates the reactivity of the enes via an appended diarylethene photoswitch. By individually tracing the conversion of the two starting chromophores to the ligation product, we evidence our color-induced photochemical switch-off system, with which bond formation between separate molecular entities can effectively be induced and halted on demand by λ_1 and λ_2. This new two-color controlled photochemical system will open new avenues for the development of multi-responsive photoresists for advanced lithographic and printing processes.



G10. Gingerol, Shogaol and Paradol: The Chemistry of Pungent Ginger Constituents

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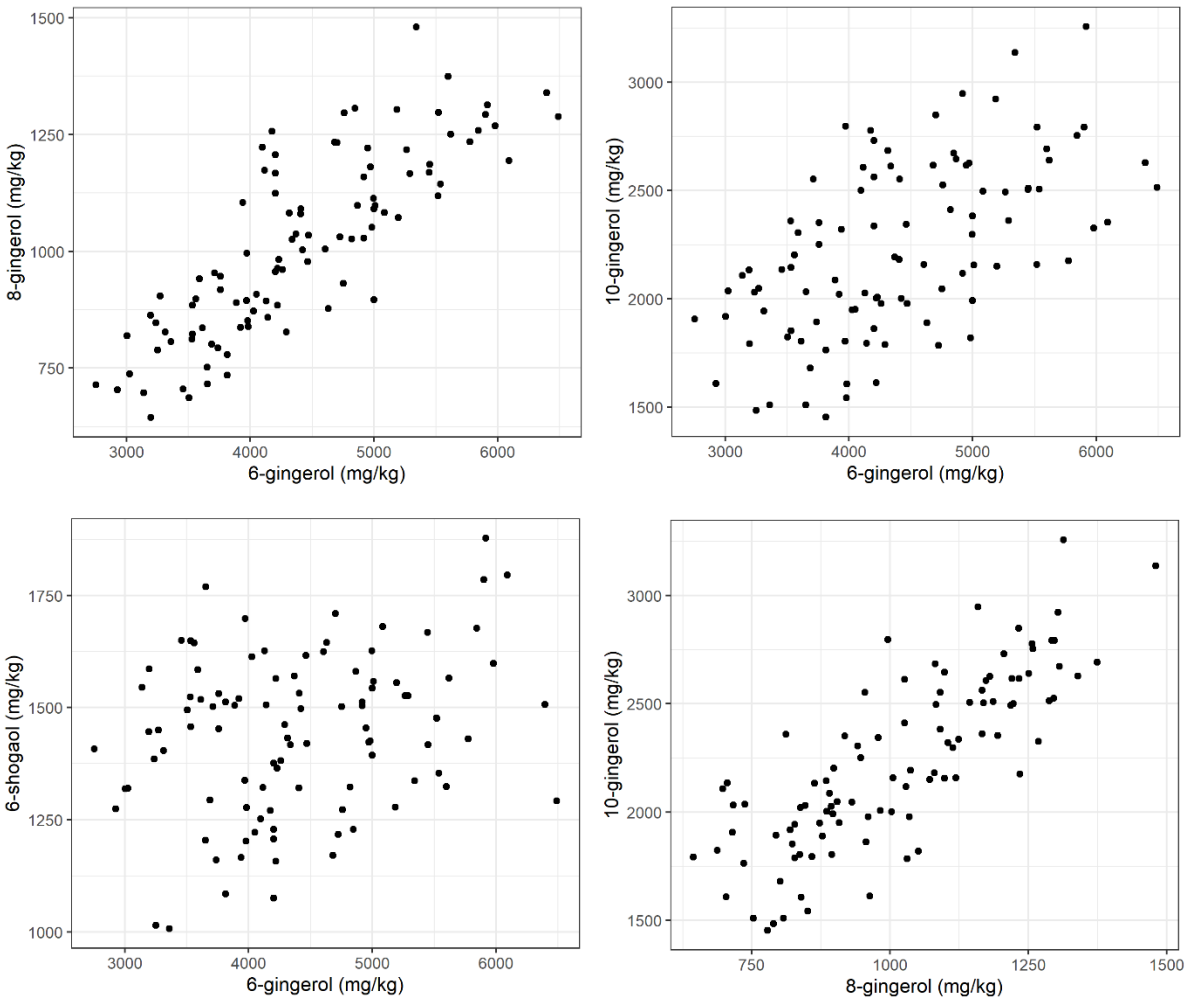
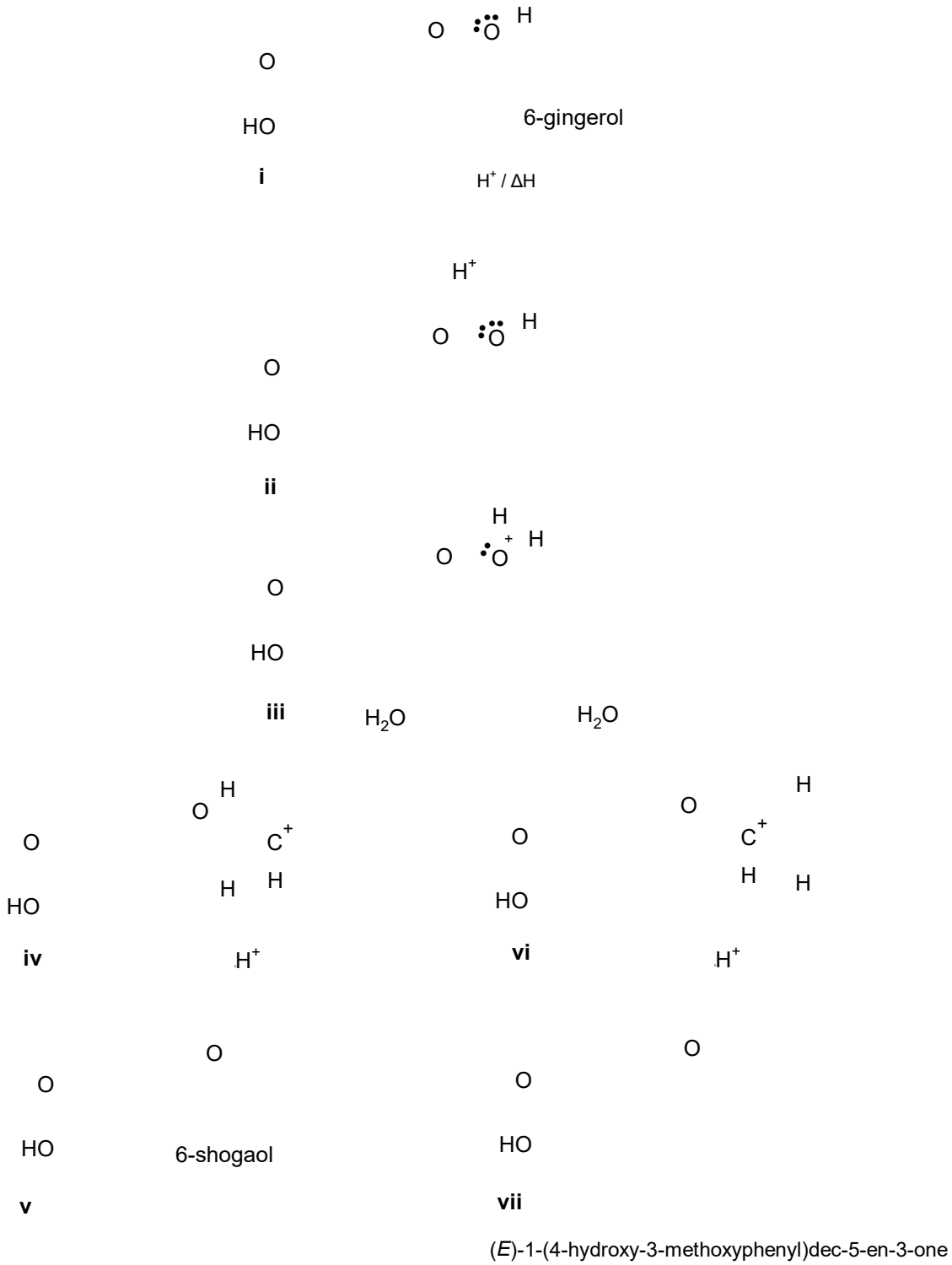
Ginger (*Zingiber officinale* Roscoe) rhizomes are well-known for their aromatic properties, being used to impart a characteristic pungent flavour to a variety of food and beverage products. The major pungent compounds are the gingerols and their derivatives, while numerous volatile compounds contribute additional aromatic flavour overtones. Ginger forms a niche crop in Australia, with a current farmgate value of $32 million; hence there is limited information available on the chemical profiles of Australian-grown ginger. We chemically profiled 100 samples of dried Queensland ginger, finding that 6-gingerol levels vary significantly depending on the growing conditions (3720-5351 mg kg^{-1}). In contrast, 6-shogaol levels were largely consistent between different samples (approximately 1400 mg kg^{-1}), suggesting that the drying process is the primary controller of the 6-shogaol content in the final product.



Scatterplots showing the relationships between the gingerol and shogaol contents in the dried ginger samples.

The proportions of 6-gingerol and 6-shogoal in the dried ginger translate to those in the subsequent wort and ginger beer products, with younger ginger samples containing a higher 6-gingerol:6-shogaol ratio. Given that several other microorganisms have been observed to convert 6-shogoal to 6-paradol, it is believed that this process would also be mediated by the ginger beer bug (actually a combination of *Saccharomyces pyriformis* and *Brevibacterium vermiforme*). However, paradol has not been identified in ginger beer to date, hence further work is required to determine the role this compound and its precursors play in determining the final organoleptic properties of ginger beer.



Reaction mechanism for the dehydration of 6-gingerol to form 6-shogoal.

G11. Characterizing the structure, bioactivity and bioavailability of active compounds from complex herbal extracts

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Many popular herbal supplements contain a very large number of natural products extracted from the plant material. Herbal and natural medicines have long been a critical part of medical practice. Medicinal plants are a rich source of bioactive phytochemicals. *Cymbopogon procerus* is a native Australian species of the family *Poaceae*. The essential oils of the plant consist of phenylpropanoids and volatile aromatic terpenes. Phenolic compounds, considered to be natural antioxidants and representing an important group of bioactive compounds, are also present in the plant.[1] In our project, we investigate the phytochemistry of *C. procerus* via extraction of plant material, fractionation of crude extract through Solid Phase Extraction (SPE) and purification of compounds using Reverse Phase High Performance Liquid Chromatography (RP-HPLC). Compounds are then identified using analytical techniques including one and two-dimensional nuclear magnetic resonance (NMR) and Liquid Chromatography Mass Spectrometry (LCMS). To date we have isolated a series of phenyl propenoid compounds, terpenes and cis-3-hexenyl- β-D-xylose.

1- Dueñas, M.; Fernández, D.; Hernández, T.; Estrella, I.; Muñoz, R., Bioactive phenolic compounds of cowpeas (Vigna sinensis L). Modifications by fermentation with natural microflora and with Lactobacillus plantarum ATCC 14917. *J. Sci. Food Agric.* **2005,** *85* (2), 297-304.

H1. The problem of pore size determination; a comparison of techniques on a commercial templated porous silica

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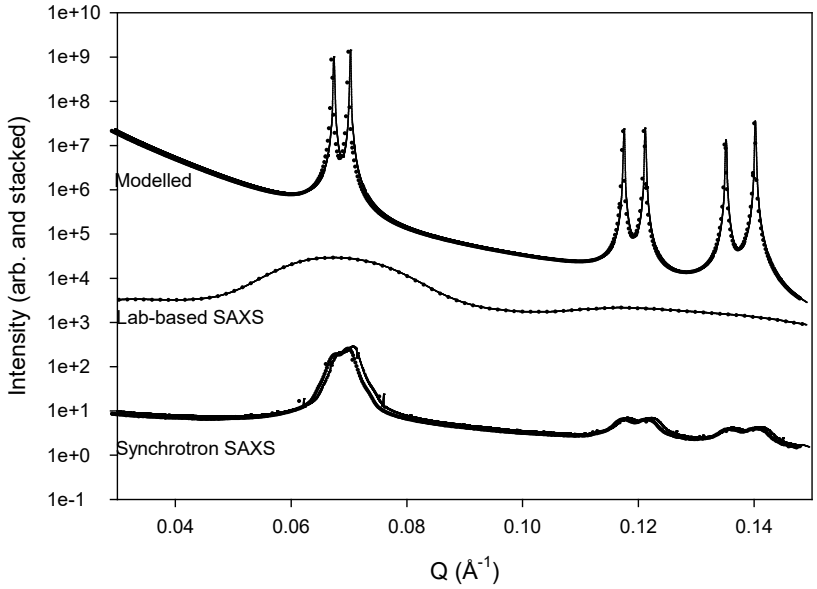
Porous materials are used widely in industry and research for applications. One of the significant factors of the functionality of porous materials is the pore size, hence it is vital to accurately determine this feature. In this study, we compare the results pore size analysis using typical N_2 adsorption isotherms, lab-based small angle x-ray scattering (SAXS) measurements and high resolution SAXS performed at the Australian Synchrotron SAXS/WAXS beamline in 2020. The SAXS/WAXS beamline received an upgrade in January of 2020 which reduced the background substantially. The diffraction pattern of MCM-41, a well-characterised and -studied templated commercial mesoporous silica with symmetry of *p6mm*, was measured, which revealed a previously unknown result of two populations of pores with a difference in unit cell parameter ***a*** of only 3.0 Å. Four literature methods are compared to derive the pore size; N_2 adsorption isotherm using the Barrett-Joyner-Halenda (BJH) method, a geometric method using the BJH and SAXS results, and a method presented by Ishii *et al.* [1] using (1) the figures presented in the article and (2) fitting Equation 17 in [1] to the experimental data. Ultimately, it is shown that each pore population has significantly different pore diameters.



Graphical abstract. A comparison of laboratory and synchrotron high resolution SAXS, and the modelled SAXS data using Eq. 17 in which can be found in [1]. A weakness of this model is that it does not convolute with the instrument resolution function. The data at a Q < 0.03 $Å^{-1}$ was cut off by the beamstop.

1. Ishii, Y., et al., *Pore Size Determination in Ordered Mesoporous Materials Using Powder X-ray Diffraction.* The Journal of Physical Chemistry C, 2013. **117**(35): p. 18120-18130.

H2. Determination of hydrogen adsorption density in porous/activated carbons at very high pressure and room temperature

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Determination of hydrogen adsorption density in porous/activated carbons at very high pressure and room temperature

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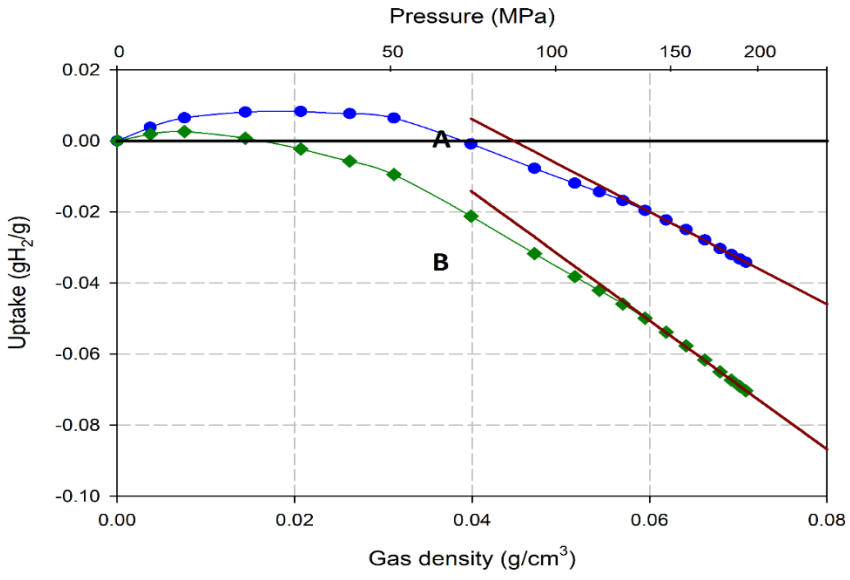
Porous materials are widely used in industrial and research applications and understanding the physical and chemical properties of these materials is often vital to optimise reactions and processes. One of the most common ways to understand porous materials is to use gas adsorption measurements, which requires accurate knowledge of several material and system parameters. Some of the parameters which accurate knowledge is required are the sample cell void volume and free gas volume, sample expansion or compression, and chemical changes including gas adsorption. For materials exhibiting IUPAC type I isotherms, the uptake saturates at high pressures and additional information about the volume (adsorption space) and density of the adsorbate can be extracted at high pressure. In this work, hydrogen isotherms are conducted at pressures up to 200 MPa at ambient temperatures and the manometric method gas uptake equations are revisited and extrapolated to high pressure. This work enabled the extraction information on the adsorbate volume and density and absolute maximum uptake of hydrogen.



Graphical abstract: Hydrogen uptake excess (plot A) and net (plot B) isotherms at 296 K to 200 MPa of an example commercial activated carbon material. Straight lines show the least squares fit to the last six points, where both plots the intercepts of these lines are 0.0280±0.0006 g, representing the maximum absolute uptake for the 0.480 g sample. From the maximum uptake (0.0280 g) and the volume of the adsorbate (0.625 cm^3), the average density of the adsorbate is 0.0447 g/cm^3.

H3. Tuning surface configuration of AgPd alloy catalysts to promote low temperature 5-hydroxymethyl-furfural oxidation

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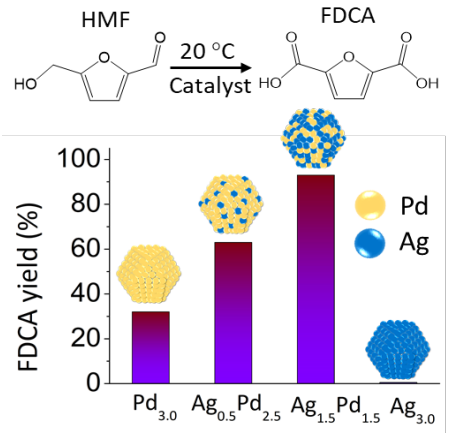
Controlling product selectivity of cascade reaction is as important as efficiency in chemical synthesis. Selective oxidation of 5-hydroxymethyl-furfural (HMF) with O_2 over a metal catalyst to yield 2,5-furandicarboxylic acid (FDCA) is a cascade reaction accompanied with side reactions. It may end with intermediate or deliver by-product. We have prepared AgPd alloy nanoparticles (NPs) on metal oxide nanofibre support as catalysts. The selectivity of the HMF oxidation over a catalyst with an Ag:Pd ratio of 1:1 can be switched simply by reaction temperature change. An excellent FDCA (cascade end product) yield can be generated at 20 °C, but 5-hydroxymethyl-2-furan carboxylic acid (HMFCA, an intermediate) as the main product is obtained at 80 °C. The surface Pd sites catalyse both the oxidation of HMF and the formation of by-products, depending on the site size and reaction temperature. The configuration of small Pd clusters segregated by small Ag clusters on the surface of spherical alloy NPs significantly accelerates the oxidation of both alcohol group to carbonyl group and carbonyl group to carboxyl groups at 20 °C without the formation of large molecule by-product. However, the side-reactions become competitive at 80 °C and impede HMFCA oxidation. The surface configuration of the alloys and reaction temperature can be optimised to selectively catalyse the oxidation of the two functional groups.



H4. Mesoporous Gold Biosensor for Electrochemical Detection of MicroRNA at Attomolar Level

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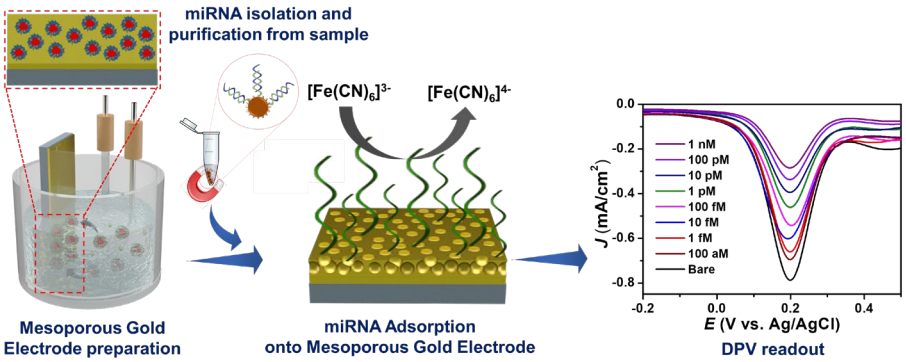
Abstract

MicroRNAs (miRNAs) being an emergent diagnostic and prognostic biomarkers for disease diagnosis, especially for cancer has appealing increasing demand for a portable, amplification-free, highly selective and sensitive detection platform.[1] Advances in nanoarchitonics render a wide variety of nanostructured electrodes with tunable shapes and surface for constructing sensitive biosensors.[2] Here we demonstrate the fabrication of a mesoporous gold (Au) based biosensor for the specific and sensitive detection of miRNA in a relatively simple and portable manner. Followed by selective isolation (magnetically), target miRNA is adsorbed directly at the mesoporous Au electrode (MPGE). The MPGE-bound miRNA is then quantified by differential pulse voltammetry (DPV) using $[Fe(CN)_6]^{4-/3-}$ redox system (Faradaic current decrease with respect to the bare MPGE).[3] This method evades the cumbersome PCR and enzymatic amplification steps. Besides, it simplifies the assay building by circumventing multiple measures tangled in conventional biosensing approaches through recognition and transduction layers. This approach attains a wide dynamic linear range from 100 aM to 1 nM with an ultra-low limit detection of 100 aM, exerting a notable augmentation in sensitivity. We envisage that this bridge of mesoporous electrode-based sensor and bio-detection sensitivity will uphold the development of high-performance detection tools for clinics.



Schematic presentation of MPGE-biosensor preparation and ultrasensitive (LOD 100 aM) detection (electrochemical) of magnetically isolated and purified miRNA.

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[3] M. K. Masud et al., *Biosens. Bioelectron*. **2020**, *168*, 112429.

H5. Development of Tyrosinase Inhibitors as Potential Anti-melanoma Agents

Wanli Jin[1], Yasir Nazir[1], Ye Yuan[1], Christian Fercher[2], Matt A. Cooper[1], Ross T. Barnard[3], Zyta M. Ziora[1], Mark A.T. Blaskovich[1]

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Abstract

Tyrosinase (TYR) is known to be rate-limiting in melanin production via conversion of L-tyrosine to L-DOPA and L-DOPA into L-dopaquinone. The melanin accumulation after long-lasting UV radiation may lead to serious dermatological and aesthetic problems and even melanoderma. TYR inhibitors can reduce the melanin biosynthesis and thus have become the basis for a new class of the therapeutics for melanoma. The study aims to investigate: (i) the structural differences between tyrosinase from different resources; (ii) the TYR inhibitory activity of the compounds via enzymatic assay using mushroom tyrosinase (mTYR); (iii) the inhibition mode of the compounds on the mTYR; (iv) the significance of developing genuine human tyrosinase (hTYR) inhibitors.

This study underlines TYR inhibitory action of the novel synthetic compounds. Because the crystal structure of hTYR has not been fully disclosed yet and hTYR and mTYR share a conserved active site, novel synthetic TYR inhibitors were screened by an enzymatic assay using mTYR. The potent candidates will be further investigated for their potential anti-tumor activity in a human melanoma skin cell line (WM164, WM1366, and D24). Some compounds which show specific targeting for mutated melanoma cells could be a tool for understanding the molecular mechanism in future studies.

References

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H6. Chemical and Biological Investigations of Australian Crinoids

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Crinoids, belong to the phylum Echinodermata, are known to produce diverse polyketide-derived pigments, which are not only responsible for their colourful appearance, but also have demonstrated activity in a range of biomedical assays.1 There are approximately 700 crinoid species that have been identified worldwide, however, only 36 species have been chemically investigated to date. Owing to our continuing interest in crinoid chemistry,2 two Australian crinoids, *Capillaster multiradiatus* and *Comatula rotalaria* were extensively investigated. Capillasterin A (**1**), a novel pyrano[2,3-*f*]chromene, together with seven known naphthopyrones (**2**–**8**) were isolated from an EtOH/H2O extract of *C. multiradiatus*. Compounds **2**–**6** were observed to display moderate to low inhibition of *in vitro* HIV-1 replication in a T cell line with EC50 values ranging from 7.5 to 25.5 µM without concomitant cytotoxicity. Chemical investigation of two specimens of *C. rotalaria* enabled the isolation of five new taurine-conjugated anthraquinones, comatulins A–E (**9**–**13**), together with 11 known (**14**–**24**) marine natural products. Ten compounds together with two additional naphthopyrone derivatives (**25**–**26**) were evaluated for their ability to inhibit HIV-1 replication *in vitro*; none of the compounds were active at 100 µM. Furthermore, a subset of the compounds was tested for nematocidal activity against *Haemonchus contortus*, which is a highly pathogenic parasite of small ruminants. The semi-synthetic compound, 6-methoxycomaparvin 5,8-dimethyl ether (**26**), showed an inhibitory effect on larval motility (IC50 = 30 µM) and development (IC50 = 31 µM) and induced the eviscerated (*Evi*) phenotype.

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H7. Discovery and Development of Novel Antimicrobial Agents Using an Open-Access Database

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Drug-resistant bacteria and fungi are some of the greatest threats to human health. Innovative strategies are needed to ensure the continued development of novel antimicrobials. Using an open-source database, CO-ADD, has led to the identification of novel compounds and existing drugs with promising antimicrobial activity. These serve as a springboard for the development of compounds with superior effect. The database was searched for activity against gram-positive and gram-negative bacteria as well as fungi. This revealed promising organoselenium hits which were chosen as a focus for further investigation. Literature precedent and CO-ADD data suggest selenium analogues of sulphur compounds show enhanced antimicrobial properties. Sulphur compounds in the database were therefore chosen for selenium substitution and will be screened for MICs against a range of gram-positive and gram-negative bacteria along with fungi.

H8. Synthesis of novel antibiotic Octapeptin derivatives against Gram-negative bacteria

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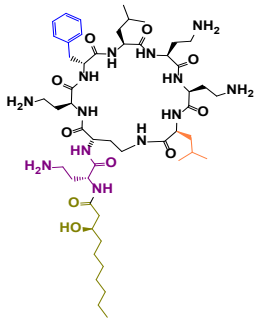
Antibiotics are the "wonder drugs" of the 20th century. We use antibiotics to treat bacterial infections and to kill bacteria without harming the patient. It has been estimated that antibiotics have extended human life expectancy by ten to twenty years. But currently, antibiotics are losing their activity against bacterial infections. The bacteria are rapidly becoming resistant to all the antibiotics that we use now. Bacteria that are not killed by antibiotics, bacteria have genes that make them resistant to antibiotics, and these genes are sharing with each other in different ways. This mutated gene help bacteria to protect themselves against antibiotics. At present days Polymyxin lipopeptides are used to treat multidrug-resistant (MDR) infections, especially in critically ill patients as last-line therapy. Unfortunately, resistance to polymyxins is also becoming widespread throughout the world. The MDR bacterial crisis has highlighted the urgent need for the discovery of novel antibiotics.



Octapeptin C4

Octapeptins have the potential to be the new generation of lipopeptide antibiotics for targeting polymyxin-resistant 'superbugs [1, 2]. Octapeptins were discovered over 40 years ago, but there is very little coverage of them in the literature, and they were discovered before the establishment of contemporary drug development processes. We have designed and synthesised novel **octapeptin** analogues to improve microbiological, pharmacological, and toxicological properties to combat Gram-negative bacteria. The preliminary results reveal that with certain modifications, a novel octapeptin analogue showed reduced cytotoxicity and significant *in-vivo* activity improvement.

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H9. Thiol addition to naturally occurring Michael acceptors: What influences reactivity?

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The design of enzyme inhibitors is one of the main research goals in medicinal chemistry. Enzyme inhibitors work by binding to a target protein to attenuate its activity. This can happen through non-covalent and/or covalent interactions. This study will focus on covalent inhibitors in drug discovery. Typically, covalent inhibitors present an electrophilic functional group capable of reacting reversibly or irreversibly with amino acid residues containing a nucleophilic group. The α,β-unsaturated carbonyl system (known as a Michael acceptor) is one of the most important reactive electrophilic functionalities. Designing selective covalent inhibitors remains a challenging task as the electrophilic groups present can act as irreversible non-selective enzyme inhibitors. Non-selectivity is generally deemed undesirable by medicinal chemists because the of the potential for side effects arising from off-target inhibition.

In this study, density functional theory calculations have been employed to investigate the fundamental features of the reactivities of naturally occurring Michael acceptors that contribute to reversible inhibition.

H10. Manganese Dioxide-based Responsive Nanoprobe for Glutathione Detection

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The development of responsive nanoprobes for biosensing and imaging of specific biomolecules are significantly contributing to the diseases' early diagnosis and treatment monitoring [1]. Glutathione (GSH) is one of the most abundant biothiols in live cells (1-10 mM in cell cytosol) that plays essential roles in many biological processes [2], such as immune regulation, oxidative stress, drug resistance, detoxification and even gene regulation. It has been reported that the abnormal levels of GSH in living organisms are associated with certain syndromes, such as leukopenia, neurodegenerative diseases, cancer, liver injury and other ailments. Therefore, a sensitive and selective probe for GSH detection is greatly important to better understand the biological roles of GSH, promoting the future (pre)clinical diagnosis and biological researches. In this study, a GSH-responsive nanoprobe (**GSH-NP**) is prepared by exploiting a manganese dioxide nanoplatform. The prepared **GSH-NP** shows good dispersibility and stability in aqueous solution. **GSH-NP** is almost non-fluorescent, while the emission can be switched on in the presence of GSH (Figure 1A). The fluorescence intensity exhibits very good linearity to the concentration of GSH (Figure 1B), which allows for the GSH detection with a detection limit of 0.77 mM. This research thus provides a reliable nanoprobe for the detection of GSH in aqueous solution.

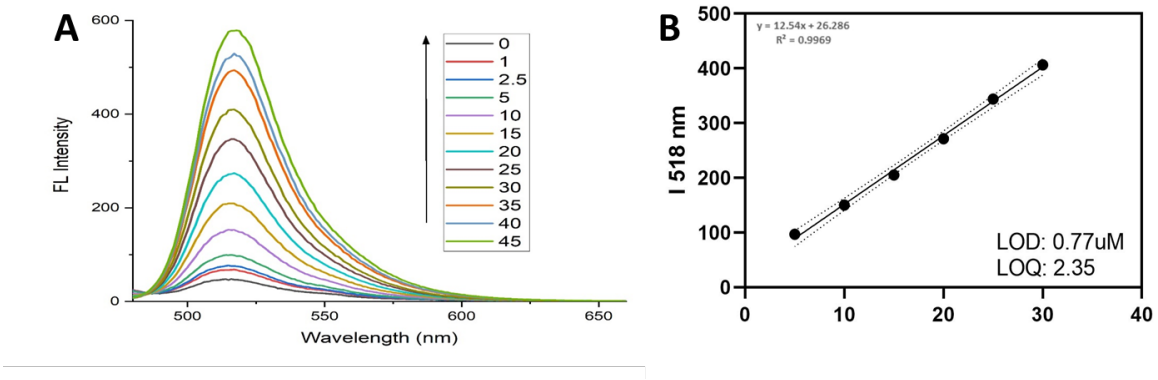

Figure 1. Fluorescence response of **GSH-NP** for GSH. (A) Changes of **GSH-NP**'s fluorescence spectra in the presence of increasing concentration of GSH. (B) The linear relationship between fluorescence intensity and GSH concentrations.

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H11. A New Test and Guidelines for the Authentication of New-World Honeys

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According to recent media reports, a large proportion of Australian supermarket honeys are adulterated. To investigate these claims, a study was undertaken using Australian honey samples obtained from shops or direct from beekeepers. Samples were analysed using the official AOAC C-4 Plant Sugars in Honey method (998.12). A proportion of both shop and beekeeper honeys appeared to be adulterated with C4 sugar - similar to the failure rates reported in the media. The AOAC test relies on the difference between the carbon isotopic composition of honey and protein precipitated from the honey. This assumes that nectar (the source of sugar) comes from the same plant species as pollen (the source of protein).

This presentation will report results for a number of experiments that demonstrated that the precipitate from Australian honeys (according to the AOAC 998.12 method) contains non-protein material where the protein component is not necessarily derived from the same plant species as the sugars. Based on these results we propose an improved method to extract protein from Australian and other New-World honey samples together with a modified acceptance criteria.

H12. Modification of chitosan for synthesis of curcumin and siRNA loaded particles for breast cancer

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Chitosan-based materials have a long history as drug delivery vehicles due to their characteristics of biodegradability, high drug carrying capability, and multi-functionality. We are working on modification of chitosan with PEG and alendronate-PEG (Ald-PEG) to make curcumin (Cur), siRNA and Cur/siRNA encapsulated particles. Low molecular weight medical grade Chitosan (Chi) was modified using EDC chemistry with PEG and Ald-PEG. Functionalization of PEG with Ald was achieved by formation of a thiol-functionalized alendronate (Ald-SH) through alendronate-Traut's reagent conjugation. Optimization of Ald thiolation as a function of pH and time of the reaction showed that a reaction time of 5 hours and a pH of 9 was optimal. PEG functionalization to Ald-SH was done through Ald-SH/maleimide-PEG-COOH coupling at pH 7. ^{1}H DOSY NMR verified coupling of this Ald-PEG to Chi with a DS of 8-15 %. The amount of EDC and NHS relative to PEG was evaluated. It was found that a higher excess (3.2x or 3.7x EDC and 2x NHS relative to PEG) had a higher yield of Ald-PEG attachment to Chi (42 or 44 %) compared to when using a twofold excess of EDC and NHS where a 30 % yield was obtained. The DS of PEG on Chi was controlled (DS = 2 to 20 %) using different molar ratios of Chi and PEG. Different degrees of substitution was also achieved at different EDC and NHS concentrations. It was found that degree of PEG substitution on chitosan is directly proportional to EDC concentration while inversely proportional to NHS concentration.

H13. Synthesis of pH-sensitive nanoparticles from degradable amphiphilic di-block copolymers, utilizing RAFT polymerisation and novel chain transfer agent

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Since the early attempts to synthesize degradable polymeric material utilizing advanced polymerization techniques, special attention has been paid towards amphiphilic block copolymers and their ability to form self-assembled nanocarriers, which can be utilized in the applications of gene and drug delivery. This direction has paved the way towards producing compatible nano-scaled polymeric delivery systems that have enhanced capabilities and versatilities when compared to their classical lipid counterparts (e.g., liposomes).

This work describes the synthesis of novel, functional macro-chain transfer agents (macro-CTA) that were used to polymerise a combination of vinyl acetate (VAc), 2-methylene-1,3-dioxepane (MDO) and vinyl bromide (VBr) co-monomers via reversible addition-fragmentation chain-transfer (RAFT) polymerisation (**Figure 1)**. These combinations were able to produce functional, degradable amphiphilic di-block copolymers that were successfully utilized in forming a number of stable, pH sensitive polymeric nanoparticles (namely, micelles and polymersomes). Different sizes and properties of these carriers were achieved by manipulating the ratios of the forming blocks, along with the particles' loads and formation conditions.

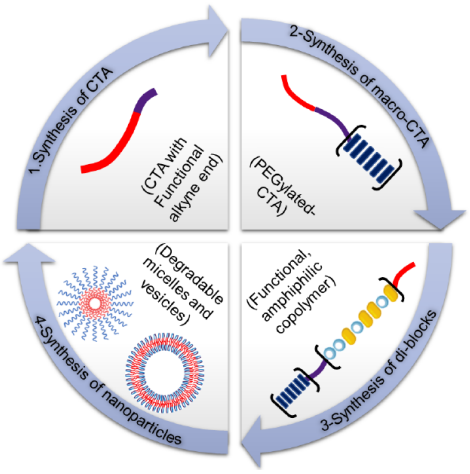

Figure 1 Mainsteps involved in the process of developing advanced nanoparticles utilizing our novel block copolymers.

Summaries of main properties obtained using a wide range of characterisation techniques are presented and discussed. Nanoparticles release profiles at different pH conditions when applied as drug delivery carriers are also illustrated and described. Our work reflects the great potentials such polymeric systems could possess when utilized to sequester anticancer drugs, once certain design factors are carefully considered and optimized.

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H14. Injectable and degradable hydrogel for post-surgical brain cancer treatment

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Glioblastoma multiforme (GBM) is the most aggressive tumour of the central nervous system. The current therapeutical approach involves surgical resection of the tumour followed by chemo and radiotherapy. The gap between surgery and chemotherapy is the main challenge in treatment and leads to a high rate of tumour recurrence. To address this limitation, we proposed an injectable hydrogel combined with PLGA-based nanoparticles (NPs) for the delivery of cancer drugs post-surgery. Alginate is biocompatible to several tissues and its properties can be improved by chemically modifying the polymer backbone. In this study we have synthesised methacrylate alginate (ALGMA) to allow *in situ* cross-links of the polymer by UV light exposure, improving the adaptability of the polymer to the surgical resection (Fig 1). The studies of ALG-MA (degree of methacrylation 20%) in artificial cerebrospinal fluidic have shown that only 40% of the hydrogel is hydrolysed within 14 days. To improve degradation rate, we have oxidised the polymer, forming methacrylate di-aldehyde alginate (OMA) gels (degree of oxidation 10%). Nanotechnology has been used to promote tissue permeation and the release of drug to infiltrative cancer cells. Variables in the fabrication process of PLGA-based NPs and drug encapsulation were investigated. In a preliminary study of PLGA NPs in agarose gel, particles have shown to be entrapped within the hydrogel network. Thus, we hypothesise that by combining NPs with a degradable network, it would promote a sustained release of the drug to the brain tissue. Studies of release strategies from this hydrogel system are ongoing.

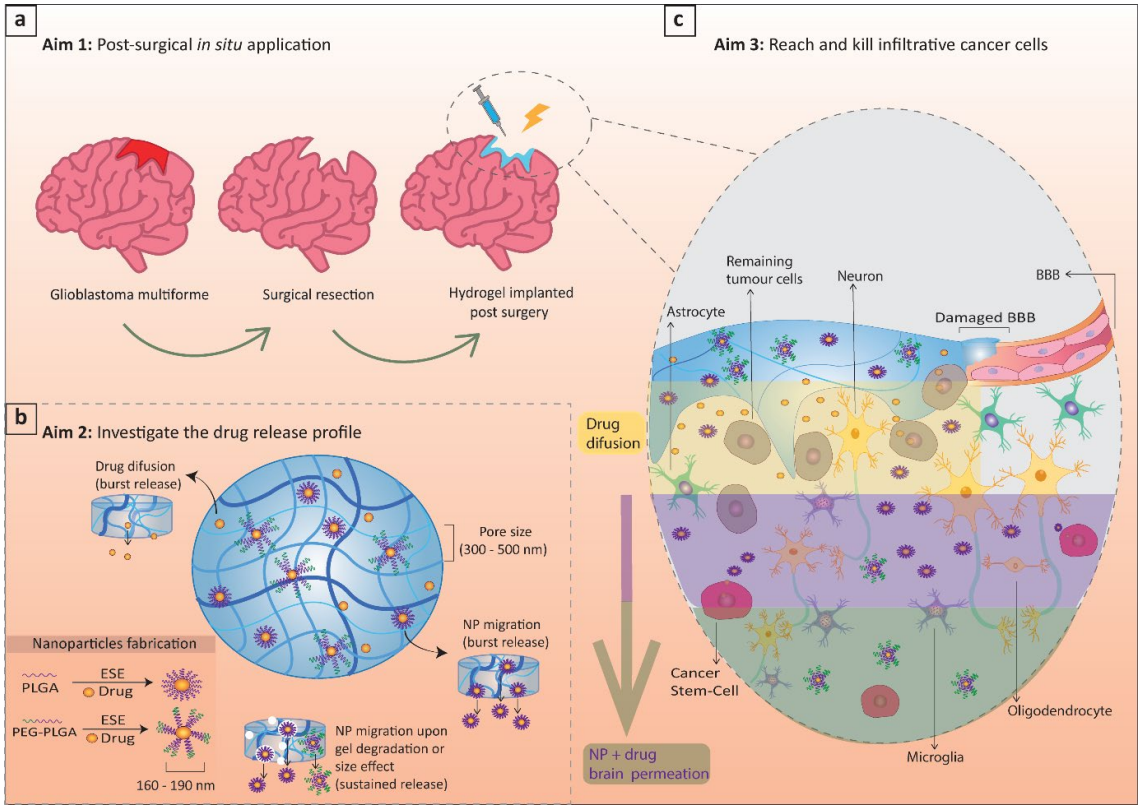

Figure 1 Diagram of hydrogel system and drug delivery strategies with the major aims of (a.) develop an injectable hydrogel, (b.) investigate various drug release profiles and (c.) improve drug permeation though the brain.

H15. Influence of simulated weathering on polypropylene microplastic properties and quantitation by pyrolysis gas chromatography mass spectrometry

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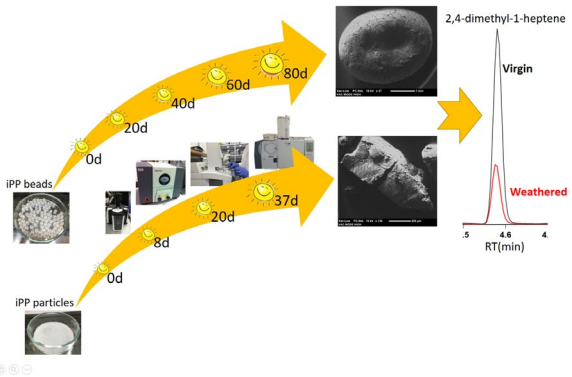
Degraded or weathered microplastics possess characteristic properties different from its virgin counterparts. However, comprehensive assessments on how these properties causes variability when quantitation analysis are performed using Pyrolysis Gas Chromatography/Mass Spectrometry (Pyr-GC/MS) are missing. This study performed accelerated laboratory weathering (0.68 W/m2) of isotactic polypropylene microplastics (iPP MPs) of two different forms, beads (size: ~5 mm, shape: oval, exposure time series: 0-80 days) and particles (size: 250-500 µm and 500-1000 µm, shape: irregular, exposure time series: 0-37 days). The photo-oxidation of the MPs was confirmed via techniques including Fourier-transform Infrared - Attenuated Total Reflection (FTIR-ATR), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). We examined whether photo-oxidation affects quantitative estimation using a double shot Pyr-GC/MS method. We further examine the differences in degree of degradation between the two forms of MPs and find weathering markers at lower pyrolysis temperature.



The degree of degradation occurred 2-fold faster for particles compared to beads, possibly due to higher surface area. Comparison of chromatograms between virgin and weathered showed no evident qualitative changes in the oligomer mixture, yet there were visible quantitative changes. Specifically, the pyrolysis product, 2,4-dimethyl-1-heptene, obtained peak areas decreasing by 50% for beads and 58% for particles (after 80 and 37 days, respectively). Six weathering markers (oxidation products) were observed to overall increase with higher exposure days. These studies suggest that weathering processes are affecting quantitation of iPP MPs using Pyr-GC/MS and highlights the need for further analytical comparisons between virgin and weathered MPs in order to avoid underestimation of MPs concentration studies

H16. Activation of Heulandite Type Zeolites to Synthesise Zeolite LTA

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Synthetic zeolite A is used in many facets of global industry, particularly as an environmentally friendly additive in detergents occupying 60% of the global zeolite market in 2019. [1]. Amid the COVID-19 pandemic, the shift in public hygiene and health awareness is predicted to be a further driver of detergent usage, predicted to drive the synthetic zeolite market to US$6.4 billion by 2027 [2]. While hundreds of synthesised zeolites have been reported, zeolite LTA has been identified as the most popular in industry by volume [3]. Production of pure starting materials are resource intensive, attracting a high cost, which has led innovative use of aluminosilicate industrial waste, such as natural zeolite, as precursors.

This study has developed an approach to synthesise zeolite LTA from three natural zeolites of differing compositions and assess the use of heat as a pre-treatment method in addition to alkali fusion. Pre-treatment by heat alone did not result in a significant increase of active monomeric ions for Escott, but was slightly more active for NextSand heat treated samples. Natural zeolite activation using alkali fusion, was necessary to depolymerise alumina and silica monomers prior to synthesis, demonstrating that zeolite A can be synthesised with reasonable purity > 82% with no other phases detected. *In situ* XRD was used to describe the transition of heulandite to heulandite-B, the dehydrated phase, compared to that of the more stable counterpart, clinoptilolite.

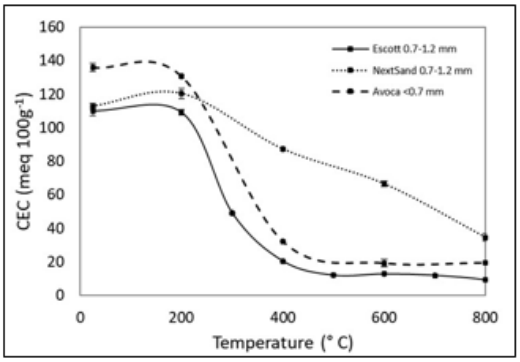

Figure 1: CEC change as a function of thermal treatment of natural zeolite samples

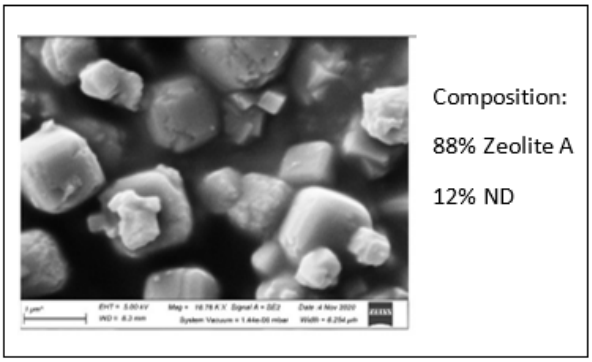

Figure 2: SEM images of synthesised zeolite LTA from fusion products

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